SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED THIN FILMS

Ph.D. thesis

Mária Darányi

Supervisor:

Dr. Ákos Kukovecz

associate professor

Department of Applied and Environmental Chemistry
University of Szeged

Szeged

2011

1. Introduction and objectives

The continuous development of science brings about smaller, faster and more accurate technological solutions of ever increasing performance. Nanostructured materials have been in the focus of particular scientific attention in the past two decades and interest in them is increasing even today. The main difference between bulk and nanostructured materials is that in the latter a considerable amount of the atoms is located on the surface of the particle which results in major changes in the physical and chemical properties of the system. This is also valid for one dimensional (1D) nanoparticles that can interact with each other for additional functional benefits and broadened scope of potential applications.

Carbon nanotubes belong to the fullerene carbon allotrope group and can be visualized either as extremely elongated fullerene molecules or as very tightly rolled-up graphene sheets. They were discovered in 1991 and have commanded considerable attention ever since. Titanate nanotubes and nanowires are formed by the recrystallization of titanium dioxide into a one dimensional trititanate framework under strong alkaline hydrothermal conditions. Originally discovered in 1998, they are under extensive scrutiny today both by the nanoscience research community and the industry because of two important features: (i) they can be prepared with close to 100 % yield in relatively simple and inexpensive reactions, and (ii) they offer versatile functionalization possibilities insofar as they can be ion exchanged in their trititanate form and they keep their one dimensional nanostructure even after thermally converting them into anatase TiO_2.

One dimensional nanostructures have been extensively studied at the Department of Applied and Environmental Chemistry recently. The synthesis, formation mechanism and some potential applications of carbon nanotubes, titanate nanotubes and nanowires were investigated before. My PhD thesis is focused on creating networks of 1D nanostructures and studying their interactions with each other. In particular, the effect of carbon nanotubes and amorphous carbon films on the photocatalytic properties of heat treated titanate nanowires is discussed in detail.

The building blocks of my thesis work were:

- Controlling the formation of amorphous carbon support layers by the addition of transition metals and carbon nanotubes
- Synthesis and characterization of titanate nanowire layers
- Synthesis and photocatalytic characterization of composite layers consisting of carbon nanotubes and TiO_2 nanostructures
- Synthesis and photocatalytic characterization of composite layers consisting of amorphous carbon and TiO_2 nanostructures

2. Experimental

Initially we synthesized amorphous carbon layers by the heat treatment of spin coated polyacrylonitryle (PAN) layers. PAN was dissolved in N,N-dimethyl-formamide and the solution was added dropwise onto a quartz disk spun at 60 rps. Carbonization was performed in N_2 flow in the 200-1000 °C temperature range in the absence as well as in the presence of transition metal salts (Co- and Ni-acetate, 0.015 – 0.200 g salt/1 g PAN) and multi-wall carbon nanotubes (MWCNTs).

Furthermore, we prepared layered structures consisting of either one dimensional anatase nanowires or Degussa P25 TiO_2 as the titanium oxide component and amorphous carbon or multi-wall carbon nanotubes as photocatalytic promotor. These layers were created by dip coating glass slides at room temperature using complex washing – coating sequences involving multiple surfactants. The prepared layers were cleaned by UV exposure (2 hours, 80 W) and annealing in air (1 hour, 300 °C).

Structural and morphological characterization was performed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) as well as X-ray diffraction, N_2 adsorption and contact angle measurements. The decomposition of the polymeric coatings was monitored by infrared and Raman spectroscopy, thermogravimetry combined with mass spectrometry and electric resistance measurement. Photocatalytic activity of the coatings was assessed in the liquid phase photodegradation reaction of methyl orange. The thickness of the catalyst layer and the progress of the photooxidation were both determined from UV-Vis spectrometric absorption measurements.

3. New scientific results

1. Results related to the chemistry of the thermal decomposition of polyacrylonitrile and the formation of well-graphitized carbonaceous coatings

1.1 We studied the details of the structural transformation of PAN in the presence of Co^{2+} and Ni^{2+} ions in the 200-800 °C temperature range which is infrequently addressed in the available literature. On the basis of our observations we were able to supplement the known PAN thermal decomposition reaction scheme by including the effect of transition metal ions on the tautomerization and aromatization steps.

1.2 We proved that the presence of Co^{2+} and Ni^{2+} ions improves the electrical conductivity of carbonized PAN layers compared to the product of the metal-free carbonization reaction performed at the same temperature. Cobalt appears to promote denitrogenation while nickel promotes dehydrogenation in PAN degradation. Overall, cobalt is more beneficial than nickel because larger graphite crystallites are formed in the presence of cobalt ions according to our Raman spectrometric measurements.

1.3 We reported the synergetic effect of multi-wall carbon nanotubes and Co^{2+} ions in the graphitization of PAN for the first time in the literature. The specific electrical resistance of carbonized PAN coatings dropped from 492 Ω/cm (unmodified coatings) to 470 and 82 Ω/cm in the presence of Co^{2+} ions and multi-wall carbon nanotubes, respectively. The specific resistance decreased further to 47 Ω/cm when PAN was carbonized together with both additives. On the basis of TG-MS evidence we suggest that the beneficial effect of carbon nanotubes could be due to the templating effect of the carbon nanotube wall on the formation of graphitic domains during PAN carbonization.

2. Results related to titanate nanowire thin films

2.1 The applicability of spin and dip coating for the preparation of titanate nanowire coatings was compared. We have found spin coated layers to be more inhomogeneous. This is due to the random obstacle induced aggregation of titanate nanowires moving radially outwards from the center of the disk.

2.2 There is no accepted literature protocol available for the SEM based assessment of the surface coverage of random networks of one dimensional nanostructures. We defined two indices of our own for this purpose and compared their performance with that of a commercial all-purpose image analysis method. The suggested new indices exhibited the same tendencies as the commercial one; therefore, the mean of these three indices appears to be a robust measure of surface coverage.

2.3 We studied the deposition of titanate nanowires on glass from tenside-free as well as from sodium dodecyl benzene sulfonate (SBDS) and poly(diallyldimethylammonium chloride) (PDDA) containing suspensions using a three level three dimensional full factorial experiment design. Based on these results we were able to suggest a general method for creating titanate nanowire coatings in a controlled way. Anionic and cationic surfactants are to be used for fine tuning surface coverages in the low and high coverage regimes, respectively. This finding can be explained by the negatively charged nature of the titanate nanowire framework.

3. Results related to sandwich composite films consisting of nanostructured carbon and titanate layers

3.1 We devised a method for creating multilayered "sandwich" structures consisting of carbon nanotubes and titanate nanowire derived anatase nanowires. Whereas spin-coated TiO_2 nanowire coatings are unsuitable for supporting further layers (see 2.1), dip-coating yields homogeneous multilayers consisting of randomly oriented TiO_2 nanowires and carbon nanotubes.

3.2 We compared the activities of Degussa P25–MWCNT–P25 and anatase nanowire–MWCNT–anatase nanowire sandwich photocatalysts in the model reaction of photocatalytic methyl orange decomposition. We have found that a thicker catalyst layer and the presence of carbon nanotubes are beneficial for the photocatalytic activity.

3.3 We have found a characteristic difference in the behavior of catalyst systems based on Degussa P25 and anatase nanowires: the activity increasing effect of carbon nanotubes dominates the behavior of thin P25 systems, whereas in anatase nanowire based systems the same effect becomes pronounced only in thick multilayers. This phenomenon could be explained on the basis of the differing morphology of the sandwich structures.

3.4 We investigated if the interaction between PAN-derived amorphous carbon coatings and TiO_2 is able to increase the photocatalytic activity of the system similarly to that observed for carbon nanotubes. The synergetic effect was observable for Degussa P25 but not in the case of anatase nanowires. This finding could also be explained on the basis of layer morphology differences.

4. Practical applicability of the results

Results related to the effects of transition metal ions on the PAN graphitization mechanism are of a fundamental research nature. However, the photocatalytically active multilayer membranes prepared by the combination of anatase nanowires and carbon nanotubes may serve as starting points for application oriented development. We consider self-supporting nanoporous filtration membranes to be their most promising field of application. The higher costs of using one dimensional nanostructures are likely to be compensated by the higher added value related to the photocatalytic self-cleaning property of the membrane.

5. Publications related to the thesis

1. **M. Darányi**, I. Sarusi, A. Sápi, A. Kukovecz, Z. Kónya, A. Erdőhelyi:
Characterization of carbon thin films prepared by the thermal decomposition of spin coated PAN layers containing metal acetates;
Thin Solid Films, accepted for publication, doi:10.1016/j.tsf.2011.06.040
IF: 1.909

2. **M. Darányi**, T. Csesznok, I. Sarusi, Á. Kukovecz, Z. Kónya, A. Erdőhelyi, I. Kiricsi:
Beneficial effect of multiwall carbon nanotubes on the graphitization of polyacrylonitrile (PAN) coatings; *Process. Appl.Cer.,* 4 (2010) 59.
IF: -

3. **M. Darányi**, Á. Kukovecz, E. Horváth, Z. Kónya, I. Kiricsi:
Fine tuning the coverage of a titanate nanowire layer on glass substrate; *Chem. Phys. Lett.,* 460 (2008) 191.
IF: 2,169

4. **M. Darányi**, T. Csesznok, Á. Kukovecz, Z. Kónya, I. Kiricsi, P. M. Ajayan, R. Vajtai:
Layer-by-Layer Assembly of TiO_2 Nanowire/Carbon Nanotube Films and Characterization of their Photocatalytic Activity; *Nanotechnology,* 22 (2011) 195701.
IF: 3,644

6. Conference presentations related to the thesis

1. **M. Darányi,** Á. Kukovecz:
Characterization of sandwiched coating layers consisting of titanate nanowires; *The Seventh Students' Meeting, "Processing and Application of Ceramics"*, Novi Sad, 2007. december 6-8. (oral)

2. **M. Darányi**, Á. Kukovecz, Z. Kónya, I. Kiricsi:
Characterization of carbon thin films prepared by the thermal decomposition of spin coated PAN films; *XXIX. EUCMOS*, Opatija, 2008. augusztus 31 - szeptember 5. (oral)

3. **M. Darányi**, Á. Kukovecz, Z. Kónya, I. Kiricsi:
Szén vékonyrétegek pásztázó elektronmikroszkópiás vizsgálata; *Magyar Mikroszkópos Konferencia,* Siófok, 2009. május 21-23. (oral)

4. **M. Darányi**, I. Sarusi, Á. Kukovecz, Z. Kónya:
Properties of carbonaceous thin films containing 1D inorganic nanoobject; *The Eighth Students' Meeting, "Processing and Application of Ceramics"*, Novi Sad, 2009. december 2-5. (oral)

7. Publications not related to the thesis

1. I. Ledneczki, **M. Darányi**, F. Fülöp, Á. Molnár:
SAC-13 silica nanocomposite solid acid catalyst in organic synthesis; *Catal. Today,* 100 (2005) 437.
IF: 2,365

2. R. Rémias, Á. Kukovecz, **M. Darányi,** G. Kozma, Sz. Varga, Z. Kónya, I. Kiricsi:
Synthesis of Zinc Glycerolate Microstacks from a ZnO Nanorod Sacrificial Template; *Eur. J. Inorg. Chem.*, 24 (2009) 1434.
IF: 2,941

3. K. Csankó, **M. Darányi**, G. Kozma, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó:
Self-assembling of Z-α-pyridylcinnamic acid molecules over polycrystalline Ag and Au surfaces followed by FT-IR and atomic force microscopies; *J. Mol. Stucture,* 993 (2011) 67.
IF: 1.599

4. D. Srankó, M. Sipiczki, É. G. Bajnóczi, **M. Darányi**, Á. Kukovecz, Z. Kónya, S. E. Canton, K. Norén, P. Sipos, I. Pálinkó:
A SEM, EDX and XAS characterization of Ba(II)Fe(III) layered double hydroxides; *J. Mol. Stucture,* 993 (2011) 62.
IF: 1.599

5. E. Nemes-Nagy, G. Kozma, **M. Darányi**, Z. Kónya, Á. Kukovecz, I. Kiricsi:
SERS szubsztrátok készítésének optimálása kísérlettervezéssel; *KeMoMo–QSAR 2009,* Szeged, 2009. április 29-30. (oral)

6. I. Ledneczki, **M. Darányi**, F. Fülöp, Á. Molnár:
SAC-13 silica nanocomposite solid acid catalyst in organic synthesis; *Nordic Symposium on Catalysis No11*, Oulu, 2004. május 23-25. (poster)

7. Á. Kukovecz, Z. Kónya, J. Kis-Csitári, M. Mohl, A. Sápi, R Rémiás, H. Haspel, **M. Darányi**, G. Kozma, I. Kiricsi:
Recent results on the synthesis and properties of 1D inorganic nanostructures; *COST 539 Action,* Aveiro, 2009. október 28-30. (oral)

8. Scientometric data

	Total	Related to the thesis
Peer-reviewed papers	8	4
Cumulative impact factor	16.226	7.722
Independent cites	18	0