Doctoral (Ph.D.) theses

Optical, structural and photoelectric properties of zinc oxide nanoparticles and hybrid thin layers

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Introduction

Results of the research of nanostructured materials and their innovative products have already been utilized in industrial application. One of the main objectives of this research is the engineering and controlling of nanodisperse systems at nanometer scale (1-100 nm), by which materials of novel properties can be produced. Colloid chemical synthesis methods open up ways to prepare nanoparticles with controlled size, high specific surface area and phases with various degree of crystallinity.

Semiconductor metal oxide nanoparticles such as zinc oxide deserve special attention because they have different morphological, optical, electric and catalytic properties depending on the preparation method. Owing to these favourable properties zinc oxide nanoparticles can be effectively utilized as gas/vapour sensors, catalysts, starting materials for antireflection coatings or in solar cells.

One of the main objectives of my research was to synthesize zinc oxide and indium ion doped zinc oxide nanoparticles with controlled size, and novel optical and structural properties in organic medium. The interfacial electric, structural and optical properties of particles were controlled by the zinc ion concentration and the indium ion/zinc ion ratio.

Zinc oxide and indium ion doped zinc oxide particles with different morphology (flower-, and prism-like structures) were prepared in aqueous medium by the so-called hydrothermal method. The aim of these experiments was to demonstrate the dependence of the emission properties on the morphology and the indium ion content of the particles.

In the second part of this work the results of the preparation of quasi 2D structures are presented. The deposition method of such thin layers exploits the colloid chemical properties of micellar systems: hexagonally aligned nanopatterns were prepared on solid substrates using diblock copolymer micellar systems. This was followed by studying of the morphological features of the nanopatterns.

Since the nature of the interactions between the nanoparticles and the polyelectrolytes, and the structure of as-formed systems are well-known in colloidal dispersions, the following objective was to learn what kind of self-assembled structures form in 2D in size range of several hundred nm, when the conditions (electrolyte concentration and pH) of polyelectrolyte solution are changed. ZnO_2/poly(acrylic acid) thin layers were prepared by layer-by-layer self assembly method using poly(acrylic acid) solutions of different NaCl-content and pH. The optical, structural and water vapour adsorption properties of the thin films were determined.

Zinc oxide/poly(acrylic acid) thin layers with controlled structure were fabricated by radio frequency magnetron sputtering technique. The optical, structural and water vapour adsorption properties of films were investigated.

To present the practical application of zinc oxide layers in the renewable energy sources, $ZnO/In_2S_3/CuInS_2$ solar cells were prepared by spray pyrolysis technique, then the optical, structural and photoelectric properties of the solar cells were determined.

Experimental

Materials

Zinc oxide and indium ion doped zinc oxide particles were synthesized by homogeneous nucleation in dimethyl sulphoxide and in aqueous medium in the presence of L-histidine by hydrothermal method, respectively. The zinc ion concentration and/or the indium ion/zinc ion ratio were varied during the syntheses.

Hexagonally aligned nanoparticles were prepared on the surface of silicon substrates from poly(styrene)-block-poly(2-vinyl-pyridine) (PS_{1350}-b-$P2VP_{400}$) diblock copolymer micellar systems in toluene by immersion method. Two different zinc salts (zinc acetate dihydrate, zinc nitrate hexahydrate) at different concentrations were applied during the preparation of the nanopatterns.

ZnO_2/poly(acrylic acid) thin layers were prepared on glass support by layer-by-layer self assembly (LbL). The films were deposited from PAA solution of different pH (5 and 6) and ionic strength (c_{NaCl}= 0- 0.1 mol/L).

ZnO/poly(acrilic acid) sandwich layers of different layer numbers (n=5, 10, 20) were produced by radio frequency magnetron sputtering. ZnO_2 was used as precursor for the sputtering of ZnO layers.

Solar cells built up from ZnO, In_2S_3 and $CuInS_2$ layers were fabricated using spray pyrolysis technique. In_2S_3 layers of different thickness served as buffer layers.

All of the starting materials were analytical or reagent grade without any further purification.

Methods

The optical properties of nanoparticles and thin layers were determined by UV-Vis spectrometry (absorption, transmission, reflection) and photoluminescence measurements.

The crystalline structure of different samples was investigated by X-ray diffraction (XRD).

Thermogravimetric (TG) and differential scanning calorimetric (DSC) measurements were used reveal the thermal behaviour of certain samples.

Low temperature nitrogen adsorption technique was applied for determination of specific surface area and porosity of zinc oxide and indium ion doped zinc oxide particles prepared by hydrothermal method.

The chemical composition of the surface of zinc oxide and indium ion doped zinc oxide particles was analyzed by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX).

For morphological investigation transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were applied.

For certain samples, the average diameter of the particles was determined by dynamic light scattering (DLS).

The interfacial electric properties of the particles and the charge of polyelectrolyte macromolecules were characterized by streaming potential and zeta potential measurements.

Viscosities of the polyelectrolyte solutions at different pHs and ionic strengths were measured by capillary viscometer at 25 ± 0.1 ^{o}C.

The build-up and the water vapour adsorption of thin layers prepared by LbL method were monitored by UV-Vis spectrometry and quartz crystal microbalance (QCM) at 25 ± 0.1 ^{o}C.

The photoelectric properties of zinc oxide and indium ion doped zinc oxide particles were measured by a source meter using interdigitated microelectrodes were applied.

Summary of the novel scientific results

T1. Effect of the zinc ion concentration and the In^{3+}/Zn^{2+} ratio on the size and optical properties of indium ion doped ZnO nanoparticles

1.a Effect of the zinc ion concentration and the In^{3+}/Zn^{2+} ratio on the size and the structure of aggregates of indium ion doped ZnO nanoparticles

Results of the TEM and DLS measurements demonstrate that the zinc ion concentration and the indium ion content have an influence on the primary particle size and on the size of the aggregates. Decrease of primary particle size with increasing In^{3+}/Zn^{2+} ratio was observed within each concentration series, which was caused by the stabilizing effect of the indium ions. It was established that the system modelled one of a basic rules of colloid chemistry, known as Weimarn's rule perfectly. At low zinc ion concentrations (0.01 and 0.025 mol/L) nuclei can grow freely, resulting in larger primary particle size and larger aggregates. At higher (0.05 és 0.1 mol/L) precursor concentrations the numerous nuclei formed hinder each other's growth resulting in smaller primary particle size and, due to the attractive interactions they form aggregates.
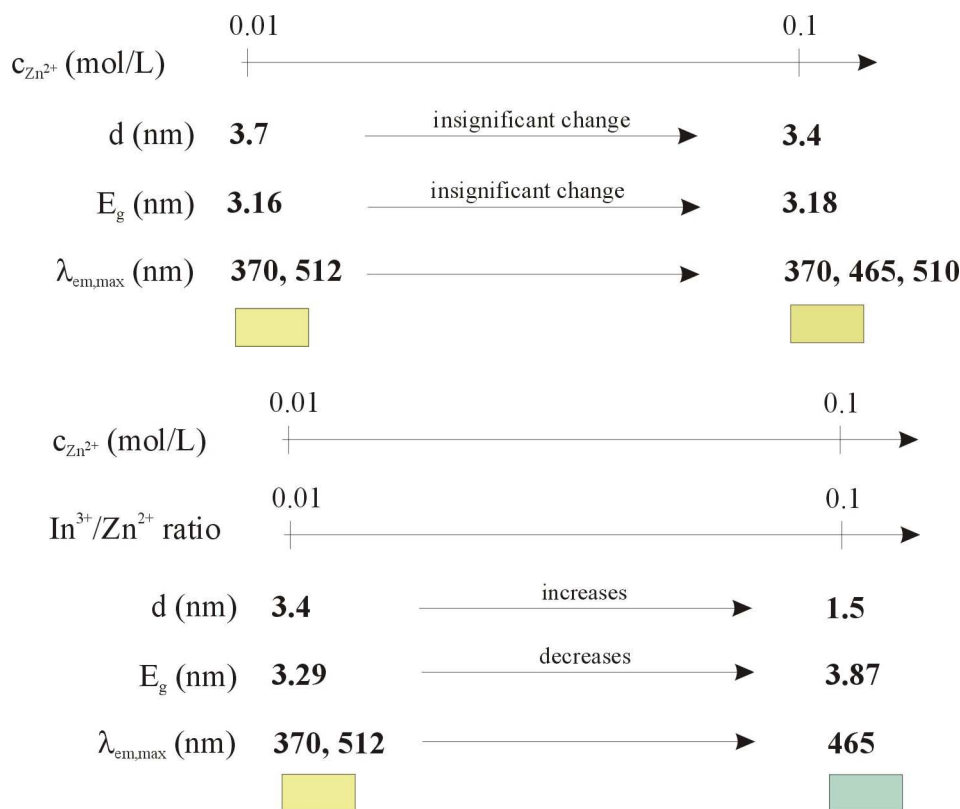
1.b Effect of the zinc ion concentration and the In^{3+}/Zn^{2+} ratio on the band gap energy of indium ion doped ZnO nanoparticles

Based on results of the UV-Vis absorption measurements it was established that the band gap energy of particles increased with the indium ion content within each concentration series. The band gap energy also increased with the zinc ion concentration when indium ion concentration was constant. It can be explained by the decrease of primary particle size and the incorporation of indium ions into the crystalline lattice of zinc oxide, which was proved by XRD and thermoanalytical measurements.

1.c Effect of the zinc ion concentration and the In^{3+}/Zn^{2+} ratio on the emission properties of indium ion doped ZnO nanoparticles

Investigation of the emission properties of different samples showed that indium ion doped zinc oxide nanoparticles had novel emission property since a new emission band located at 465 nm appeared in their emission spectra. The emission intensity of the new band

increases with the indium ion concentration. The appearance of this new emission band and the increase of its intensity can be explained by the generation of interstitial Zn defects in the crystalline lattice and the increase of the concentration of those defects caused by the incorporation of indium ions, respectively.

$c_{Zn^{2+}}$ (mol/L) 0.01 ——————————————————— 0.1 →

d (nm) 3.7 ——— insignificant change ———→ 3.4

E_g (nm) 3.16 ——— insignificant change ———→ 3.18

$\lambda_{em,max}$ (nm) 370, 512 ————————————————→ 370, 465, 510

$c_{Zn^{2+}}$ (mol/L) 0.01 ——————————————————— 0.1 →

In^{3+}/Zn^{2+} ratio 0.01 ——————————————————— 0.1 →

d (nm) 3.4 ——— increases ———→ 1.5

E_g (nm) 3.29 ——— decreases ———→ 3.87

$\lambda_{em,max}$ (nm) 370, 512 ————————————————→ 465

Change of primary particle size, band gap energy values and emission maxima of particles with zinc ion concentration and indium ion/zinc ion ratio

T2. Colloid chemical properties of ZnO and indium ion doped ZnO particles controlled by complex formation

2.a Effect of the In^{3+}/Zn^{2+} ratio on the morphology and structure of indium ion doped ZnO particles

Based on the results of TEM and SEM studies it was found that the original morphology of ZnO particles distorted due to the doping with indium ions for both series (flower-, and prism-like series). The surface analytic measurements (XPS, EDX) showed that the surface of the particles enriched in indium ions. Moreover, the distribution of those species is not homogeneous, which is caused by the specific adsorption of indium ions on the defects of the crystalline surfaces.

2.b Effect of the In^{3+}/Zn^{2+} ratio on the band gap energy of indium ion doped ZnO particles

Owing to the increasing indium ion concentration, a red shift of UV diffuse reflection spectra was observed in case of both series of different morphology. This indicates the decrease of band gap energy, which can be explained by the appearance of a new donor energy level in the valence band of the ZnO. The new donor level originates from the incorporation of indium ions to the crystalline lattice.

2.c Effect of the In^{3+}/Zn^{2+} ratio on the photoemission properties of indium ion doped ZnO particles

Results of the photoluminescence measurements showed that the morphology and the indium ion content of the samples influenced the emission characteristics of the samples. In the emission spectrum of the flower-like undoped ZnO particles a wide emission band located at 565 nm in the green-yellow region can be found, while the prism-like undoped ZnO particles emit in the green region at 509 nm. Both emission bands shift towards shorter wavelengths with the indium ion concentration, while their intensity significantly increases. The shift of the visible emissions originates from the different chemical environment of the oxygen vacancies (V_o^+). The increase in emission intensity could be associated with increasing concentration of oxygen vacancies.

T3. Preparation of nanopatterns from diblock copolymer micellar systems

3.a Effect of the precursor concentration on the size of the micellar cores

AFM measurements proved that the loaded PS_{1350}-b-$P2VP_{400}$ micelles aligned hexagonally on the surface of silicon substrate. The average distance between the micellar cores is 98.6 nm, which does not change significantly with the type and the concentration of zinc salts. It was concluded that the structure of the nanopatterns could not be controlled by the concentration of zinc salt, but the chemical structure of the polymer chains. The height of the cores slightly increases with the concentration of precursor salts. The height of micellar cores were higher than when zinc nitrate hexahydrate was used. It can be explained by the higher crystal water content of zinc nitrate, which made the polar core more extensively swollen.

3.b Effect of the precursor concentration on the size of the particles

It was established that from the results of AFM measurements the optimal loading for the zinc nitrate hexahydrate was 0.3, where the particles reached their maximum height (3.5 ± 0.5 nm). Zinc acetate dihydrate afforded smaller particles; the average height of the particles varies between 0.9 and 1.8 nm independently from the loading factor. The average diameter of the particles, determined form the XRD patterns using the Scherrer equation, varies between 17-25 nm independently from the precursor concentration. It can be explained both by the adhesion forces between the support and the zinc precursor, and the interfacial surface tension, which could deform the original hemispherical shape during the oxygen plasma treatment, giving particles with lens like morphology.

3.c Chemical composition of the particles

The aim of the above experiments was to prepare hexagonally aligned ZnO nanoparticles. However, structural investigations (XPS, XRD) evidenced that both zinc precursor salts reacted with the oxide layer on the surface of the silicon substrates forming Zn_2SiO_4 instead of ZnO nanoparticles. This phenomenon is explained by the presence of small amounts of water in the micellar cores.

T4. Optical, morphological and adsorption properties of ZnO_2/poly(acrylic acid) hybrid thin films prepared by layer-by-layer self-assembly method

4.a Effect of the conformation of poly(acrylic acid) chains on the optical and morphological properties of ZnO_2/poly(acrylic acid) films

The build-up of ZnO_2/poly(acrylic acid) thin layers – deposited by layer-by layer self-assembly from poly(acrylic acid) solution at different NaCl concentration and pH– was monitored by UV-Vis spectrometry, AFM and QCM techniques. It was found that the structure of the films was not affected by the pH in the studied range, the amount of material adsorbed on the surface of the substrate is proportional with the number of immersion cycles and the layer thickness of the films increased with the electrolyte concentration. Deposition from media free from electrolyte renders thin polymer layers due to the stretched conformation of highly charged chains (ζ= -19.2 mV). In the presence of NaCl in the

polyelectrolyte solution the polymers fold up and their charges are progressively screened by the counter ions (ζ= -4.8 mV). Therefore, the number of trains decreases resulting in the formation of a thick adsorption layer. AFM measurements verified that the surface roughness of the films increased with the electrolyte concentration, which also indicates the aggregated structure of polyelectrolyte.

4.b Effect of the conformation of poly(acrylic acid) chains on the water vapour adsorption properties of ZnO$_2$/poly(acrylic acid) films

Water sorption isotherms of the films (n=5, 10, c_{NaCl}=0 mol/L at pH=5 and n=5, 10, c_{NaCl}=0.5 mol/L at pH=5) were determined by QCM and UV-Vis reflection measurements at different relative pressures of water vapour. The isotherms determined by QCM were characterized by distinct hysteresis loops, which give clear evidence for the porous nature of the hybrid multilayers. The pore size distribution functions revealed that the respective average pore diameters of films deposited from media containing no added NaCl (c_{NaCl}=0 mol/L) ranged from 5 to 8 nm, while the films prepared at pH = 5 and c_{NaCl} =0.05 mol/L were more porous with smaller pore diameter (d=3-6 nm). The monomolecular coverage, specific surface area and porosity of films increase with the electrolyte content. The UV-Vis reflection measurement is also a suitable method for the monitoring of water vapour adsorption since the reflection spectrum of films shifts towards higher wavelengths due to the adsorption process. This shift becomes more significant when relative pressure of water vapour increases. The shift can be explained by the increase of the effective refractive index of the films. This phenomenon makes the ZnO$_2$/poly(acrylic acid) films feasible for optical sensor application.

T5. Optical and structural properties of ZnO/poly(acrylic acid) thin films prepared by radio frequency magnetron sputtering

5.a Band gap energy of the ZnO/poly(acrylic acid) thin films

The band gap energy value of films at different layer numbers determined by Tauc relationship decreases with increasing layer thickness (3.40 eV, 3.39 eV and 3.36 eV at n=5, 10 and 20). It is caused by the increase of particle size of ZnO.

5.b Emission property of the ZnO/poly(acrylic acid) thin films

These films show visible emission. This visible emission shifts towards shorter wavelengths, while its intensity decreases with the layer thickness (at n= 5, 10 and 20 it is located at 669 nm in the red region, at 575 nm in the green-yellow region and at 531 nm in the green region, respectively). The shift of the band can be explained by the heat treatment of the films – at ~ 120 ^{o}C for different times during the deposition–, whereas the concentration of the Zn and O defects (Zn_i and V_o^+) in the crystalline lattice changes. Decrease of intensity is explained by the increasing concentration of defects.

5.c Structure of the ZnO/poly(acrylic acid) thin films

Cross sectional SEM images confirmed the formation of a real sandwich structure, as the films built up from thicker ZnO layers (~ 60 nm) and thinner PAA layers (~30 nm). Film thicknesses determined from the SEM images (430 nm, 640 nm and 1450 nm, when n=5, 10, 20) are in accordance with the thicknesses calculated form the reflection spectra (423 nm, 622 nm and 1426 nm, when n=5, 10, 20).

5.d Water vapour adsorption property of the ZnO/poly(acrylic acid) thin films

Investigation of the water vapour characteristic of ZnO/poly(acrylic acid) thin films showed that the films had dense, non porous structure, therefore the films are not able to adsorb large amounts of water vapour. For this reason the films can not be utilized as optical sensors such as the ZnO_2/poly(acrylic acid) thin films prepared by LbL method.

T6. Photoelectric properties of ZnO/In$_2$S$_3$/CuInS$_2$ solar cells

Photoelectric investigations revealed that the thickness of the In$_2$S$_3$ buffer layer had a great influence on the photoelectric properties of ZnO/In$_2$S$_3$/CuInS$_2$ solar cells; the short circuit current, and the open circuit voltage nearly doubled, while the maximum power and the efficiency increased threefold when the thickness of buffer layer was doubled. This can be explained by the formation of a real p-n junction device, in which the buffer layer can contribute better to the generation of photocurrent.

Scientific publications

Publication related to the scientific topic of the dissertation

1. **Edit Pál**, Imre Dékány
Structural, optical and photoelectric properies of indium-doped zinc oxide nanoparticles prepared in dimethyl sulphoxide
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 318(2008) 141-150
IF_{2007}: **1,601**

2. **Edit Pál**, Albert Oszkó, Petra Mela, Martin Möller, Imre Dékány
Preparation of hexagonally aligned inorganic nanoparticles from diblock copolymer micellar systems
Colloids and Surfaces A: Physicochemical and Engineering Aspects, 331 (2008) 213-219
IF_{2007}: **1,601**

3. **Edit Pál**, Torben Seemann, Volker Zöllmer, Matthias Busse, Imre Dékány
Hybrid ZnO/polymer thin films prepared by RF magnetron sputtering
Colloid and Polymer Science, in press
IF_{2007}: **1,62**

4. **Edit Pál**, Dániel Sebők, Viktória Hornok, Imre Dékány
Structural, optical and adsorption properties of ZnO_2/poly(acrylic acid) hybrid thin porous films prepared by ionic strength controlled layer-by-layer method
Journal of Colloid and Interface Science, in press
IF_{2007}: **2,309**

5. **Edit Pál**, Viktória Hornok, Albert Oszkó, Imre Dékány
Hydrothermal synthesis of prism-like and flower-like ZnO and indium-doped ZnO structures
Colloids and Surfaces A: Physicochemical and Engineering Aspects, accepted for publication
IF_{2007}: **1,601**

ΣIF: **8,732**

Other publications

6. Szilágyi István, **Pál Edit**, Horváth László, Labádi Imre
Az N-hidroxietil-glicin kölcsönhatása fémionokkal
Magyar Kémiai Folyóirat, 2 (2005) 83-87
IF: -

7. Labadi I, **Pal E**, Tudose R, Costisor O
Thermal behaviour of complexes antipyrine derivatives – part III.
Journal of Thermal Analysis and Calorimerty 83 (2006) 681-686
IF_{2006}: **1,438**

ΣIF: **10,17**

Lectures and posters in international conferences

1. **E. Pál**, V. Hornok, I. Dékány
Investigation of fluorescent CdS, ZnO, and Cd doped ZnO nanolayers prepared by LBL method
20th Conference of the European Colloid and Interface Society and 18th European Chemistry at Interfaces Conference, September 17-22, 2006, Budapest, Hungary, (Poster), Abstract of papers: p. 391.

2. **E. Pál**, K. Szabó, R. Kun, I. Dékány
Adsorption and photocatalytic degradation of acridin orange on TiO_2/layer silicate nanocomposites
20th Conference of the European Colloid and Interface Society and 18th European Chemistry at Interfaces Conference, September 17-22, 2006, Budapest, Hungary, (Poster), Abstract of papers: p. 422.

3. **E. Pál**, V. Hornok, I. Dékány
Investigation of fluorescent ZnO and CdS /polymer and Cd doped ZnO /polymer hybrid nanolayers and their photocatalytic activity
12th IACIS International Conference on Surface and Colloid Science, October 15-20, 2006, Beijing, China, (Poster), Abstract of papers: p. 125.

4. I. Dékány, R. Kun, **E. Pál**, L. Kőrösi, K. Szendrei, D. Sebők
Optical and photocatalytical properties of ZnO and ZnAl double hydroxide nanoparticles stabilized in ultrathin films by LBL method
12th IACIS International Conference on Surface and Colloid Science, October 15-20, 2006, Beijing, China, (Poster), Abstract of papers: p. 22.

5. Imre Dékány, Rita Patakfalvi, **Edit Pál**
Preparation, stabilization and rheological properties of CdS, ZnS and silver nanodispersion
2nd Vienna Iternational Conference, Micro- and nano Technology, 14-16, March, 2007, Vienna, Ausrtia, (Lecture), Abstract of papers: p. 181-185

6. I. Dékány, **E. Pál**, V. Hornok, T. Aradi, D. Sebők
Nanostructured ultrathin hybrid layers prepared by LBL method.
COST D43 Meeting, Cracow, Poland, 18-21 March, 2007. (Lecture)

7. A. Majzik, R. Patakfalvi, **E. Pál**, D. Sebők, I. Dékány
Surface functionalisation and self-assembly of metal oxide and gold colloids
21th ECIS Conference, 10-15. Sept, 2007. Geneve, Switzerland, (Poster), Abstract of papers: p. 330.

8. **Edit Pál**, Imre Dékány
Preparation and investigation of In^{3+}-doped ZnO fluorescent nanoparticles
9th Conference on Colloid Chemistry, October 3-5, 2007, Siófok, Hungary, (Lecture), Abstract of papers: p. 22

9. **Edit Pál**, Dániel Sebők, László Janovák, Imre Dékány
Self-assembled hybrid nanostructured films
Workshop of Cost action D 43 „Functionalizes materials and Interfaces", April 2-4, 2008, Berlin, Germany, (Poster)

10. **E. Pál**, A. Oszkó, P. Mela, M. Möller, I. Dékány
Preparation of hexagonally aligned inorganic nanoparticles from diblock-copolymer micellar systems
22nd ECIS Conference and Workshop of Cost action D 43, August 31-September 05, 2008, Cracow, Poland, (Poster), Abstract of papers: p. 595.

11. D. Sebők, L. Janovák, **E. Pál**, I. Dékány
Adsorption and reflection properties of functional hybrid nanofilms
22nd ECIS Conference and Workshop of Cost action D 43, August 31-September 05, 2008, Cracow, Poland, (Poster), Abstract of papers: p. 606.

12. Dániel Sebők, **Edit Pál,** Róbert Kun, Tamás Szabó, Judit Ménesi, Andrea Majzik, Viktória Hornok, Imre Dékány
Functional and reactive surfaces prepared by layer-by-layer assembly of nanohybrid materials
22nd ECIS Conference and Workshop of Cost action D 43, August 31-September 05, 2008, Cracow, Poland, (Lecture), Abstract of papers: p. 58.