Theses of Ph.D. dissertation

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Preparation and characterization of functional nanostructured thin layers composed of silica, ZnO and core/shell silica/ZnO particles

French-Hungarian joint doctorate

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Introduction

Today's technology has to aim at the environmental conscious development with new, environmentally friendly processes and materials. Nanotechnology presents eligible solutions to the challenges of modern materials science. It deals with small amount of matter (e.g. thin film), which – by its nanostructure and/or unusual composition – provides traditional bulk materials with new or improved functionalities. The concept of multifunctional materials and the use of solar energy have arisen, also, in the scope of energy-saving.

The degradation of organic pollutants by photocatalysis is a suitable solution for industry. It is based on the intense contact between the pollutant and the surface of a catalyst material (e.g. TiO_2 semiconductor) susceptible to generate oxidizing species upon photon absorption. The mineralization of the organic compounds occurs in surface reactions; therefore, thin layer catalysts with high surface to volume ratio are desirable. Multifunctional membranes were already designed for complex wastewater treatment (separation and purification in one step) using mesoporous titania top layer in an ultrafiltration membrane.

Zinc oxide is a semiconductor material of industrial interest due to its semiconducting, photovoltaic, sorption etc. properties. Its photocatalytic activity is comparable to that of titania. Furthermore, ZnO is chemically active towards H_2S gas (ZnO transforms into ZnS upon chemisorptions of toxic hydrogen sulphide). Thus, the fabrication of ZnO-based multifunctional membranes for the coupling of ultrafiltration with photocatalysis or Gas Separation with chemisorption can be of industrial interest.

Antireflective coatings are means of energy saving, too. They can reduce losses in transmitted light e.g. in laser optics. Otherwise, antireflective coatings are used on glass surfaces for the comfort of eyes (lenses, displays, windscreens). ZnO is not suitable for the preparation of antireflective coatings in homogeneous thin layers because of its high refractive index (2.01). Nevertheless, a well adapted structure of the high refractive index ZnO and a small refractive index material like silica (1.45) may show gradient refractive index providing antireflectivity. The Langmuir-Blodgett method – previously used for the deposition of antireflective coatings using silica nanoparticles – offers full control of the resulting film structure by its rigorous layer-by-layer proceeding.

Aim of the work

The aim of the present work was to elaborate multifunctional nanostructured thin layers for possible application as a) self-cleaning antireflective coating and b) active top layer on porous ceramic membranes coupling separation and photocatalysis or separation and chemisorption.

Methods

Two colloidal chemistry routes were used for the preparation of thin layers, the Langmuir-Blodgett (LB) technique (**a**) and the dip coating technique (**b**). Each technique presented here separately involved several steps from the preparation of sols to the deposition and drying of the films.

(**a**) The main steps of film preparation by the Langmuir-Blodgett technique were the preparation of a nanoparticulate sol (1), the formation of Langmuir film at the air-water interface (2) and the transfer of the interfacial monoparticulate layer onto the surface of a solid substrate (3).

(1) Two synthesis procedures were chosen from the literature for the preparation of relatively narrow size distribution ZnO organosols with mean particle diameter of 3 nm (Meulenkamp, 1998) and respectively between 110 nm and 410 nm (Seelig et al., 2003).

(2) The structure of Langmuir films prepared from ZnO particles at the air-water interface was studied by in-situ techniques (surface pressure (Π) - surface area (A) isotherms, Brewster angle microscopy and scanning angle reflectometry) and an ex-situ technique (transmission electron microscopy). The effect of purification or solvent exchange of the ZnO sols and the addition of surfactant or silica particles on the resulting layer structure was investigated. Optical parameters of interfacial layers were obtained by model fitting on reflectance vs. angle of incidence curve.

(3) The deposition of ZnO Langmuir films on the surface of solid substrates was achieved by the Langmuir-Blodgett technique (**Figure 1**). Mono-and multilayered films were designed from identical particles. A new concept was the fabrication of complex LB films by alternate deposition of silica and ZnO particulate layers. Mixed LB films of nearly the same size silica and ZnO particles were fabricated as another novelty from corresponding Langmuir films.

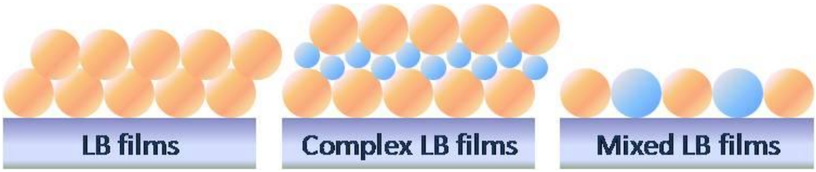

Figure 1: Concept of nanopartculate LB films, complex LB films and mixed LB films.

The structure of the films was studied by scanning electron microscopy. The optical properties of ZnO films were studied by UV-Vis spectroscopy, ellipsometry and X-ray reflectometry measurements. The optical properties of complex LB films (average refractive index, thickness, inhomogeneity factor) were evaluated by UV-Vis spectroscopy and optical model fitting. Photcatalytic activity of the LB films was tested in contact with methyl orange aqueous solution ((5.5 $mg.L^{-1}$)). The mechanical stability of the films towards ethanolic ultrasonication was investigated after three methods of surface modification, heat treatment, coating with silica ultrathin films (tetraethyl orthosilicate precursor) and the creation of siloxane bridges

(3-methacryloxypropyl(trimethoxy)silane precursor) between the particles and the substrate.

(**b**) Dip coating technique involved the preparation of a precursor sol (1), which was deposited on the surface of solid substrate by dip coating or slip casting (2). The stabilization and strengthening of the films was achieved thereafter by heat treatment (3).

(1) A concentrated aqueous core/shell silica/ZnO sol was elaborated using LUDOX HS40 commercial silica sol of 12 nm mean particle diameter. The ethanolic ZnO sol with 3 nm mean particle diameter was adapted for dip coating. Organic binders were dissolved in both of them to obtain precursor sols. Electrophoretic mobility measurements were carried out on model silica suspensions in order to confirm the surface modification of silica by Zn_{II} species.

(2) Thin films were deposited from aqueous and ethanolic precursor sols on the surface of glass slides and macroporous alumina substrate by dip coating. Slip casting of the aqueous precursor sol on the inner side of porous alumina tubes gave rise to ceramic membranes.

(3) The materials dried at room temperature were slowly heated to 150 °C and, finally, annealed at 500°C to eliminate organic binders and complete the transformation of Zn_{II} species into ZnO in the case of the core/shell hydrosol. The structure, composition, crystallinity and porosity of the elaborated materials were investigated by scanning electron microscopy, energy-dispersive X-ray

spectrometry, X-ray diffraction, thermogravimetric analysis and N_2 adsorption/desorption. Membrane properties of the tubular ceramic membrane were assessed in a tangential filtration device at fixed circulation speed (2.7 $m.s^{-1}$). The transmembrane pressure was varied in the range of 1-6 bar. Photocatalytic activity of the films was tested in contact with methylene blue aqueous solution (38 $mg.L^{-1}$) or solid stearic acid. Preliminary experiments on coupling separation and photocatalysis were carried out in a diffusion cell. The chemisorption ability of ZnO-based materials was tested on powders. X-ray diffraction, thermogravimetric analysis and N_2 adsorption/desorption techniques confirmed the complete transformation of ZnO into ZnS and the regeneration of ZnO.

Results

1. It was shown that ZnO nanoparticles synthesized by the procedure of Seelig contain important porosity (30-40%). The N_2 adsorption, ellipsometry, scanning angle reflectometry and pycnometry measurements revealed that the porosity is partially closed (10-25%). This finding and the morphology of particles visualised by transmission electron microscopy provide indirect evidences about the aggregation growth mechanism of particles.
2. New method for the preparation of concentrated hydrosol of core/shell silica/ZnO nanoparticles (350 mg.mL^{-1} solid content) was elaborated. The increased stability of the sol at pH 5.4 compared with silica hydrosol and electrophoretic mobility measurements demonstrated the formation of ZnO shell around the silica cores (**Figure 2**).

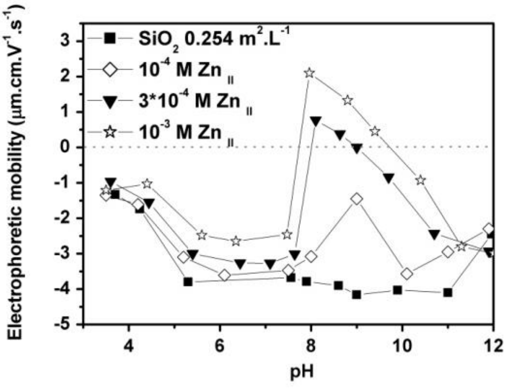

Figure 2: Electrophoretic mobility of ~400 nm diameter silica particles in Zn_{II} solutions. The charge reversal of silica particles at certain Zn_{II} concentrations is unambiguously observed.

3. Langmuir films of ZnO nanoparticles in a broad range of particle sizes were successfully prepared at the air-water interface.
    a) The spreading ability of 3 nm diameter ZnO particles was improved by adding appropriate amount of chloroform and arachidic acid into the prepared organosol. This finding was attributed to the stabilization effect of additives which was revealed by dynamic light scattering measurements.
    b) The larger, nearly monodisperse and spherical shaped ZnO particles (in the 110-410 nm diameter size range) could be spread successfully without surfactant additive. The spreading ability of the particles was greatly improved by transferring them into chloroform. In these cases water contact angles of ZnO particles were estimated from the non-dissipative part of surface pressure (Π) vs. surface area (A) isotherms and from scanning angle reflectometry measurements. Contact angles from the completely different methods were in a reasonable agreement to each other (33°, 34°, from the isotherms and 27°, 29° from reflectometry for 172 nm and 267 nm diameter ZnO particles, respectively) and showed partially wettable ZnO nanoparticles. The results also confirm the previously suggested hypothesis about the possibility of contact angle determination from the non-dissipative part of Π - A isotherms obtained for nanoparticulate Langmuir films.

c) This was the first attempt in the literature to prepare mixed Langmuir films from nearly the same size (~100 nm diameter) silica and ZnO nanoparticles. Segregation of different type particles in the Langmuir films was observed in transmission electron micrographs below ZnO/silica particle number ratio of ≈ 3. Additionally, significant cohesiveness of the mixed films was evidenced during repeated compression-decompression of the Langmuir films. This reveals important colloid and/or capillary interactions among the silica and ZnO nanoparticles at water-air and water-spreading liquid interfaces.

4. New experimental method was developed for the preparation of multifunctional, complex LB films of ZnO and silica nanoparticles on the surface of glass, quartz, conductive (ITO) glass and silicon substrates by the consecutive deposition of ZnO and silica layers.

   a) The six- and nine-layered complex LB films (composed of 3 nm diameter ZnO particles and 37 nm diameter silica particles) showed both antireflective properties and photocatalytic activity (multifunctional coating). Both properties mainly depended on the layer sequence (**Figure 3**). The best transparency was the result of decreasing ZnO content in the film from the substrate to the air. On the contrary, the photocatalytic activity of the LB films was more important with increasing ZnO content from the substrate to the air, **Figure 4**).

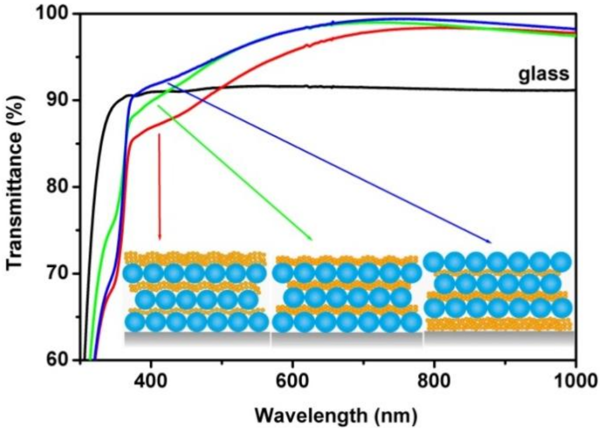

Figure 3: Transmittance spectra of the nine-layered complex LB films with different layer sequence. The antireflective property of the complex films is clearly demonstrated.

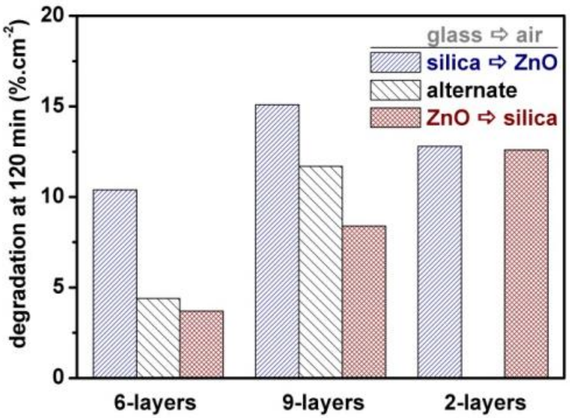

Figure 4: Layer sequence-dependent photocatalytic activity of complex LB films. The increasing ZnO quantity from the substrate to the air is marked in blue, the increasing silica quantity from the substrate to the air is marked in red.

b) For the study of the complex LB film structure transmittance spectra were computed by the *gradient refractive index* optical model which was fitted to the experimental spectra. The resulting inhomogeneity factors unambiguously confirmed the desired structure of the films.

5. The LB films of 110-410 nm diameter ZnO particles show antireflectivity as a consequence of high particle porosity and special LB structure. In addition angle-dependent coloured reflection is observed (**Figure 5**). The antireflective wavelength region is slightly broadened by incorporating silica particles in the same LB layer (mixed films) or by depositing them independently under or over the ZnO LB layer (two-layered complex films). The effect of layer sequence was notable in the optical properties (gradient refractive index), but it was not significant for the photocatalytic activity of these films (**Figure 4**).

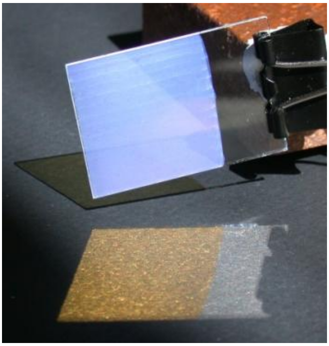

Figure 5: Photograph of monolayered LB film of 267 nm diameter ZnO particles in sunlight.

6. The mechanical stability of the silica LB films was greatly improved by a chemical reaction creating siloxane chains between the particles and the substrate surface. A moderate improvement in the mechanical stability of ZnO and two-layered complex LB films was achieved by the same method. The latter proves the formation of chains between ZnO and silica particles. The surface modification induced a slight decrease in the transmittance of the films, but did not reduce their photocatalytic activity.
7. Multifunctional ceramic membranes were prepared for the coupling of separation with photocatalysis and separation with chemisorption.
    a) The porous texture (mean pore diameter = 6 nm) and permeability properties (membrane permeability = 7.4×10^{-20} m^2, Molecular weight cut-off = 53 kDa) show the adequacy of tubular ceramic membrane for ultrafiltration (**Figure 6**).

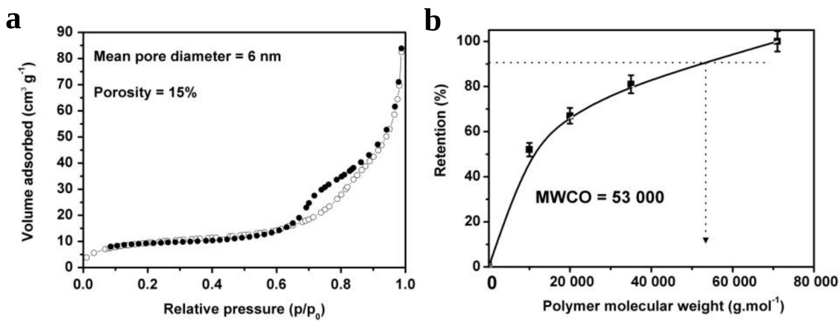

Figure 6: a) N_2 adsorption/desorption isotherm of tubular ceramic membrane. b) Determination of the molecular weight cut-off of the tubular ceramic membrane from the retention of different molecular weight polymers.

b) The photocatalytic activity of the ZnO-based flat membrane was quantified estimating the destroyed MB per surface area of macroporous support = 1.5×10^{-9} mol.s^{-1}.m^{-2} (**Figure 7**).

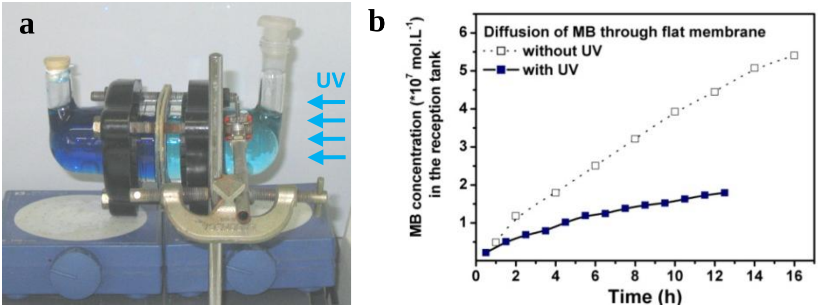

Figure 7: Diffusion of methylene blue across macroporous membrane coated with silica/ZnO core/shell material. a) Photograph of the cell composed of a feed tank filled with 10^{-4} mol.L^{-1} methylene blue (MB) aqueous solution, the flat membrane and the reception tank filled initially with distilled water. b) Evolution of MB concentration in the reception tank with and without UV irradiation.

c) The ZnO content of the silica/ZnO core/shell material was completely transformed into ZnS within one hour at 500°C under H_2S flow, and the regeneration of the membrane material was achieved at 600°C in air.

Theses

1. Recently developed, combined experimental methods were used to evidence the high porosity of 110-410 nm diameter ZnO particles fabricated with the method of Seelig. (Paper 5)
2. New method was elaborated for the preparation of concentrated hydrosol of core/shell silica/ZnO nanoparticles. (Papers 3 and 8)
3. ZnO particles at the air-water interface (Papers 2 and 5):
    a. *New method was elaborated for the spreading of ZnO nanoparticles by choosing proper composition of spreading liquid and an appropriate amount of surfactant molecule.*
    b. *It was shown that the two independent methods developed earlier for the contact angle estimation of silica particles were applicable for ZnO nanoparticles.*
    c. *Unexpectedly high cohesiveness and segregation of nearly the same size silica and ZnO particles were found for their mixed Langmuir films.*
4. New procedure was developed for the preparation of multifunctional complex LB films. (Papers 4, 5 and 6)
    a. *The six- and nine-layered complex LB films (composed of 3 nm diameter ZnO particles and 37 nm diameter silica particles) showed both antireflective properties*

and photocatalytic activity. Both properties mainly depended on the layer sequence in the film.

b. *The resulting parameter values of the optical model fitted to the experimental UV-Vis transmittance spectra unambiguously confirmed the desired structure of the films.*

5. The ZnO particles fabricated by the method of Seelig gave rise to inherently multifunctional LB films showing both antireflective effect and photocatalytic activity. Fine-tuning of transmittance was achieved by the incorporation of nearly the same size silica particles in the ZnO LB films (mixed and complex LB films). (Paper 5)

6. The mechanical stability of silica and ZnO particulate LB films was considerably increased by the adaptation of a chemical surface modification procedure. (Paper 5)

7. Multifunctional ceramic membranes were prepared for the coupling of separation with photocatalysis and for the coupling of separation with chemisorption. (Papers 1, 3 and 8)

Possible applications

The thin films prepared during this *thesis* work were designed for possible application as a) antireflective self-cleaning coatings and b) top layers on porous ceramic membranes coupling separation with photocatalysis and separation with chemisorption.

a) The LB films prepared from ZnO nanoparticles with improved mechanical stability are recommended for applications comforting eyes (window and windscreen coatings etc.) because of the UV absorption of ZnO.
b) The ceramic membranes are proposed for wastewater treatment because of the easy scaling-up of tubular filtration units.

Publications

Papers – Book chapters

1. F. Bosc, L. Naszályi, A. Ayral: An example of innovative strategies in the application and the design of ceramic membranes: the photocatalytic membranes, p. 66-97, G. Nechifor and M. Barboiu Eds., Editura Printech, Bucharest, 2007.

Papers – Journal articles

2. L. Naszályi, A. Deák, E. Hild, A. Ayral, A.L. Kovács, Z. Hórvölgyi: Langmuir-Blodgett films composed of size-quantized ZnO nanoparticles: Fabrication and optical characterization, Thin Solid Films, 515 (2006) 2587-2595. IF(2006): 1.666

3. L. Naszályi, F. Bosc, A. El Mansouri, A. van der Lee, D. Cot, Z. Hórvölgyi, A. Ayral: Sol-gel derived mesoporous SiO_2/ZnO active coating and development of multifunctional ceramic membranes, Separation and Purification Technology, 59 (2008) 304–309, IF (2006): 2.497

4. E. Hild, A. Deák, L. Naszályi, Ö. Sepsi, N. Ábrahám, Z. Hórvölgyi: Use of the optical admittance function and its WKB approximation to simulate and evaluate transmittance spectra of graded-index colloidal films, Journal of Optics A: Pure and Applied Optics 9 (2007), 920-930. IF (2006): 1.604

5. L. Naszályi Nagy, N. Ábrahám, A.L. Kovács, A. van der Lee, V. Rouessac, D. Cot, A. Ayral, Z. Hórvölgyi: Zinc oxide LB flms with improved antireflective, photocatalytic and mechanical properties, Progr. Coll. Polymer Sci, accepted for publication, IF (2006): 1.249

6. L. Naszályi Nagy, N. Ábrahám, Ö. Sepsi, E. Hild, D. Cot, A. Ayral, Z. Hórvölgyi: Complex Langmuir-Blodgett films of SiO_2 and ZnO

nanoparticles with advantageous optical and photocatalytical properties, Langmuir, submitted, IF (2006): 3.902

Papers – Conference proceedings

7. A. Deák, L. Naszályi, Z. Hórvölgyi: Preparation and characterization of particulate Langmuir-Blodgett films, 4th International Conference on Research and Education, Inter-Academia 2005, Wuppertal, Germany, Proc. Vol. 2 p. 603-608.

8. L. Naszályi, F. Bosc, A. Ayral, Z. Hórvölgyi: Multifunctional mesoporous membranes synthesized using ZnO/SiO_2 core-shell nanoparticles, 9th International Conference on Inorganic Membranes (ICIM9), Lillehammer, Norway, 2006, Proc. p. 232-235.

Oral presentations

9. L. Naszályi, V. Feuillade, A. Deák, Z. Hórvölgyi and A. Ayral: Couches minces nanocristallines d'oxyde de zinc préparées par voie sol-gel, Grand Journée Sud-Ouest, Montpellier 2005, oral presentation

10. R.Cs. Tóth, N. Ábrahám, A. Deák, L. Naszályi, A. Ayral, F. Bosc, Z. Hórvölgyi: Fabrication of antireflective and self-cleaning coatings by wet colloid chemical methods, Veszprém 2006, oral presentation

11. L. Naszályi, F.-R. Bosc, A. Ayral, Z. Hórvölgyi: Multifunctional mesoporous membranes synthesized using ZnO/SiO_2 core-shell nanoparticles, 9th International Conference on Inorganic Membranes (ICIM9), Lillehammer 2006, oral presentation

12. L. Naszályi, F. Bosc, Z. Hórvölgyi, A. Ayral: Colloidal routes for the preparation of multifunctional ceramic membranes, 20th ECIS Conference, Budapest 2006, oral presentation, Abstr. 07.01

13. Z. Hórvölgyi, A. Agod, I. Bársony, A. Deák, N. Nagy, L. Naszályi, R. Tóth: Nanoparticulate coatings: optical, photocatalytic and

wettability properties, HUNN Nyári Iskola, Balatonfüred, 2007, oral presentation, Abstr. p.13.

14. L. Naszályi, A. Deák, A.L. Kovács, A. Ayral, Z. Hórvölgyi: Cink-oxid részecskék szintézise és felhasználása Langmuir-Blodgett típusú filmek előállítására, HUNN Nyári Iskola, Balatonfüred, 2007, oral presentation, Abstr. p.30.

15. L. Naszályi, R. Cs. Tóth, A. Deák, A van der Lee, V. Rouessac, Z. Hórvölgyi, A. Ayral: Sol-gel synthesis of ZnO-based thin layers with enhanced optical properties, XIVth International Sol-Gel Conference, Montpellier 2007, oral presentation, Abstr. p 158.

16. L. Naszályi, N. Ábrahám, Z. Hórvölgyi: Stabilized Langmuir-Blodgett films of nanoparticles for photocatalytic application, 2nd European COST 540 WG1 Seminar on LIGHT SOURCES AND NEW NANOSTRUCTURES FOR PHOTOCATALYSIS, Toulouse, 2007, oral presentation

17. L. Naszályi Nagy, A. Ayral, Z. Hórvölgyi: Multifunkciós Langmuir-Blodgett-filmek cink-oxid és szilika nanorészecskékből, Oláh György Doktori Iskola Konferenciája, Budapest 2008, oral presentation

18. L. Naszályi Nagy, A. Ayral, Z. Hórvölgyi: ZnO-alapú multifunkciós nanorétegek előállítása és jellemzése, presentation of thesis work, Session of the Working Group on Colloidal Chemistry and Materials Science of HAS, Siófok, 2008, oral presentation

Poster presentations

19. L. Naszályi, Z. Hórvölgyi: Preparation and characterization of nanostructured layers composed of ZnO nanoparticles, Interacademia 2004, Budapest, poster presentation

20. V. Feuillade, L. Naszályi, Z. Hórvölgyi, A. Ayral : Preparation and characterization of ZnO nanostructured and nanoporous layers, Symposium E, Strasbourg 2005, poster presentation

21. A. Deák, L. Naszályi, Z. Hórvölgyi: Preparation and characterization of particulate Langmuir-Blodgett films, 4th International Conference on Research and Education, Inter-Academia 2005, Wuppertal, poster presentation

22. L. Naszályi, N. Ábrahám, A. Deák, A.L. Kovács, A. Ayral, E. Hild, Z. Hórvölgyi: Preparation and characterization of nanoparticulate Langmuir-Blodgett films with gradient refractive index, 20th ECIS Conference, Budapest 2006, poster presentation, Abstr. P6.23

23. R. Tóth, L. Naszályi, J. Szira, F. Bosc, A. Ayral, Z. Hórvölgyi: Wetting Properties of Nanoparticulate Langmuir-Blodgett Films, 20th ECIS Conference, Budapest 2006, poster presentation, Abstr. P6.36

24. L. Naszályi, N. Ábrahám, A.L. Kovács, P. Baranyai, D. Cot, A. Ayral, Z. Hórvölgyi: Post modification of Langmuir-Blodgett films of znO nanoparticles for improving their mechanical and chemical stability, 9th Conference on Colloid Chemistry, Siófok 2007, poster presentation, Abstr. p. 136.

25. L. Naszályi, N. Ábrahám, Z. Hórvölgyi: Stability experiments on multifunctional nanoparticulate coatings, Kolozsvár, 13th Vegyészkonferencia 2007, Erdélyi Magyar Műszaki Tudományos Társaság, Kolozsvár, Roumania, 2007, poster presentation