Doctoral (Ph. D.) theses

Optical and photoluminescence properties of two-dimensional ordered zinc oxide nanostructures

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Introduction and aims

Synthesis of nanostructured materials and the study of their novel properties are governing increasing number of scientific research. The materials structured on the nanometer scale have found new applications in many fields, but they are perhaps the most important components in the state-of-the art technologies. If the nanosized materials are applied as a coating of a bulk material, they can add functionality over the existing structural properties. Beside the individual properties of the nanoparticles, the overall features are determined by the structure (2D or 3D) in which they are assembled. Appropriate ordering of the nanosized particles can result in novel optical properties which can not be observed on case of bulk materials or randomly ordered particles. A nice example is the photonic crystal, where the periodicy in the nanometer size range results in the appearance on the photonic band gap.

In the last decades several new methods were developed for the contolled synthesis and self-ordering of nanoparticles. Methods were developed for the preparation of monodispersed, spherical particles of various materials, where the point is that the size, the shape and the surface properties of the individual particles have to be as identical as possible. This is important, because perfect arrangement can only be achieved only with identical particles. The colloid crystals have already found wide range of applications: two-dimensional structures can be used as masks for litography, the three-dimensional structures are to be applied for optical sensors due to the photonic properties, biological and medical applications target the detection of different peptides, DNA or bacteria and additionally these structures can be used as model systems for the study of different physical phenomena.

During my work I was amied at the formation of ordered, two-dimensional films, for which monodispersed and spherical buliding blocks of ZnO were synthesized. Different methods were used for the preparation of the ordered films: Langmuir-films at the air water interface, the Langmuir-Blodgett film transfer of these floating monolayers onto various substrates. The important advantage of Langmuir-Blodgett (LB) technique is the possibility of layer by layer film formation, which allows high control of the final structure. Beside these techniques tempate assisted alignment of the ZnO particles was also realized. After the elaboration of the structural and oprical properties of particles I was aimed at the study of the optical properties of their supported films.

ZnO nanoparticles synthesized in the size range of 3-7 nm were characterized as a function of their size-dependent optical and photoluminescence properties, which was followed by the demonstration of the emission properties of their single and multilayered Langmuir-Blodgett films. I have prepared hybrid nanostructured films composed of ZnO and Au in order to investigate the effect of the plasmonic coupling between the metal and the semiconductor on the emission properties of the ZnO films. The enhanced emission of the fims could be applied in the field of sensor development, like the metal enhanced fluorescence based detection.

The monodispersed, spherical ZnO particles synthesized in the size range of 200-500 nm are perfect buliding blocks for ordered two-dimensional structures. My goal was to develop an optical model and fit the measured UV-Vis reflectance spectra in order to describe the optical behaviour of the ZnO Langmuir-Blodgett films. This model allows to calculate film thickness and effective refractive index of the films, which can be used in the future as the detection mechanism of gas sensors. I have also prepared patterned assemblies of these particles by means of template assisted self-assembly, the aim was to characterize their special optical and photoluminescence fatures and compare it with the LB films.

Materials and methods

I have applied two methods for the synthesis of nearly monodispersed ZnO particles in two size ranges of different orders of magnitude.

I. ZnO nanoparticles with average size in the 3-7 nm range were obtained by the basic hydrolysis of zinc acteate dihydrate in ethanolic media [*Meulenkamp et al, 1998, J Phys Chem B*].

- ♦ Size of the particles was characteized by means of UV-Vis absorbance spectra, transmission electronmicroscopic (TEM) images and dinamic light scattering (DLS). Crystallinity of powder samples were analyzed by X-ray diffraction method, Scherrer equation was used for the determination of crystal size. Photoluminescence emission measurements were performed for the characterization of size-dependent emission properties.
- ♦ Langmuir-films at the air/water interface were studied by the measurement of surface pressure vs. surface area isotherms in a Kibron MicroTroughS type Langmuir trough.
- ♦ Langmuir-Blodgett technique (Fig. 1.) was used to transfer the floating Langmuir monolayer onto solid substrates. The structure of the films was visualized by AFM images, optical properties were studied by UV-Vis absorbance spectra, emission properties were evaluated by photoluminescence emission measurements.

- ♦ Au coated substrates were also used for the Langmuir-Blodgett film preparation. Two types of Au coatings were used: (i) spray coating of 10 nm average sized Au nanoparticles on quartz surface or (ii) continuos 50 nm thick film of Au. Stearic acid Langmuir-Blodgett layers were inserted between the metal and the semiconductor in order to study the effect of their distance on the interaction. The ZnO-Au hybrid films were charcterized by means of XRD, UV-Vis absorbance and photoluminescence measurements.

II. ZnO particles with the average size in the range of 200-500 nm were synthesized by the hydrolysis of zinc acetate dihydrate in diethylene glycol media in autoclave [*Jezequel et al, 1994, Mat. Sci. Forum*].

- ♦ Size and morphology of the particles was characterized with transmission electronmicroscopic (TEM) and scanning electronmicroscopic (SEM) images, XRD measurements were performed for the determination of the crystal structure, nitrogen adsorption and desorption measurements were carried out for BET specific surface area, porosity and particle density determination.
- ♦ Langmuir-films at the air/water interface were formed, surface pressure vs. surface area isotherms were measured for obtaining information on interfacial behaviour and ordering.
- ♦ Single and multilayered Langmuir-Blodgett films (Fig. 1.) were obtained with consecutive transfer of the floating monolayers onto different solid substrates. Film structure and particle ordering was demonstrated with SEM images. Optical properties were characterized by means of UV-Vis transmittance, reflectance and photoluminescence emission measurements.

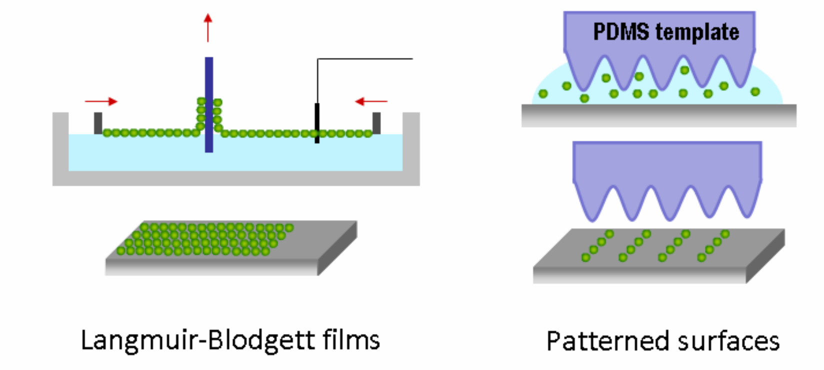

Fig. 1. 2D particle assembly techniques used in this work.

♦ Quartz and Au coated substrates were used for the patterned assemblies of the monodispersed ZnO particles (Fig. 1.). Optimization of the assembly process involved the simultaneous variation of the surface properties of the substrate, the particles and the template, the structural parameters of the template and the concentration of the ZnO dispersion. Particle ordering on the patterned surface was demonstrated on SEM images. The characteristic periodicity of the pattern was determined with SEM images and with laser diffraction measurements. Optical measuements were performed to characterize UV-Vis transmittance and photoluminescence emission properties.

Summary of the new scientific results

T1. *Ostwald ripening, stabilization and size-dependent photoluminescence emission properties of ZnO particles synthesized in ethanol in the size range of 3-7 nm*

a./ ZnO particles in ethanolic media undergo Ostwald ripening at room temperature, which means that the larger particles continue to grow due to the higher solubility of smaller ones. This process was followed by UV-Vis absorbance measurements: the shift in the absorbance band and the calculated size values showed that average particle diameter incerases from 3 nm to 7 nm in a 10 day period. I have succesfully applied PEI (polyethyleneimine) as steric stabilizer, the syntesis of the particles in the presence of PEI resulted in smaller average particle size (~2.5 nm). Additionally I have shown that low temperature storage can also greatly hinder the aging of the sol whithout addition of any stabilizing agent.

b./ Photoluminescence emission spectra of the particles showed a strong and wide visible emission and a weak and sharp UV emission. I have found that PEI coating on the particle surface results in the enhancement of the visible emission and the quenching of the UV emission. This can be explained by the competitive processes of the two emissions: PEI facilitates the the relaxation of the excitons through surface defects (leading to increased visible emission) and therefore hinders the direct recombination process (results in quenched UV emission). The slow increas in the particle size allowed me to determine size-dependent photoluminescence properties (Fig. 2.). Both the bare and the PEI coated particles demonstrated red shift in the emission maxima with increasing size, approximately 30 nm shift could be observed.

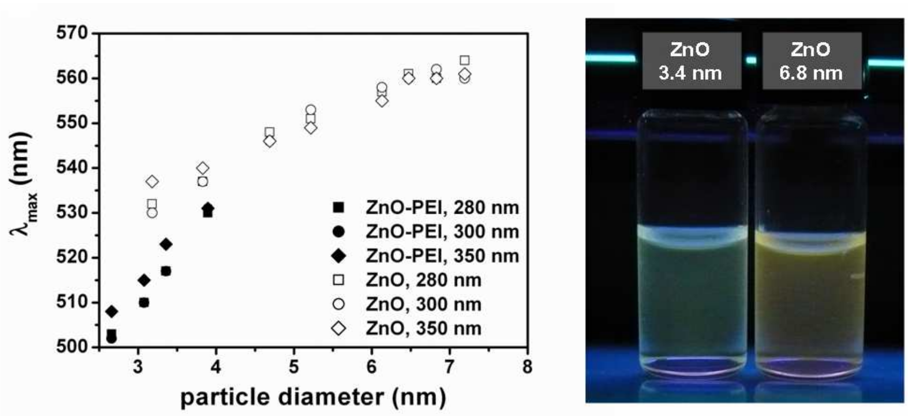

Fig. 2. a) Size-dependent photoluminescence emission properties of ZnO particles (with different excitation sources) b) Colours of the emission of different sized ZnO particles.

T2. *Langmuir-film formation and interfacial behaviour of ZnO particles of average size in the range of 3-7 nm*

Study of the spreading and interfacial behaviour of the ZnO and PEI-coated ZnO particles revealed succesful film formation and transfer onto solid substrates. I have found that the particles form a film with relatively high cohesivity due to their small size and high surface energy, structure of the films is domain-like. During the compression a remarkable portion ofthe PEI coated particles leave the interface into the subphase due to the good solubility and hydration of the polyelectrolite, which can be seen on the isotherms. All the same it is possible to form the compact floating monolayer and transfer it onto solid substrates.

T3. *Fluorescence emission properties of the Langmuir-Blodgett films of ZnO particles with average size in the 3-7 nm size range.*

a./ Fluorescence emission study of the single and multilayered Langmuir-Blodgett films of ZnO particles on quartz showed that the bare and PEI coated particles preserve their emission properties in their films. The etanolic dispersion of the unmodified ZnO particles showed a weak UV and a strong visible emission, their films show the visible emission, but the UV emission is quenched. The PEI stabilized particles exhibit only the strong visible emission which appears with a slight shift in their films. The emission spectra of the single and multilayered films are very similar, slight increase in the emission intensity was found with increasing layer numbers.

T4. *Demonstration of plasmonic interactions in hybrid films of ZnO (3-7 nm) and Au*

The plasmonic interaction in the Au-ZnO hybrid films was evaluated by photoluminescence emission measurements: change in both the position and in the intensity of the emitted light (Fig. 3.) was found. The structure of the gold plays a dominant role in the interaction: spray coated film of 10 nm sized Au nanoparticles caused smaller shift and weaker enhancement compared to the 50 nm thick continuous film of Au. The reason can be the difference in the local electic filed around the metal due to plasmon resonance or it can be due to the difference in the amount of the gold in the films (the mass of Au at a surface unit is higher in the continuous film).

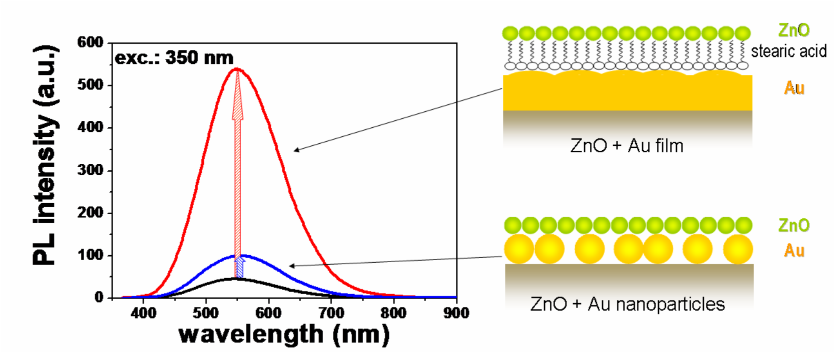

Fig. 2. Photoluminescence emission enhancement due to plasmonic interactions in Au-ZnO hybrid films.

The stearic acid Langmuir-Blodgett layers insetrted between the metal and the semiconductor act as spacers, varying layer numbers of the fatty acid makes possible to obtain information about the distance dependency of the Au-ZnO interaction. In case of the 50 nm continuous films the greatest enhancement (12-fold) was found with one spacer layer (2.2 nm distance form XRD measurements) and the largest shift (7 nm) with 2 layers (4.4 nm). In case of the spray coated Au film the largest enhancement was observed with direct contact (no spacer layer) and the largest shift with 1 spacer. The mechanism responsible for the change in the emission characteristics is the metal enhanced fluorescence. During this process the enhanced local electric field (present due to the interaction) results in the increased quantum effiiency, which appears as enhanced emission.

T5. *Observations on the synthesis and structural properties of monodispersed, spherical ZnO particles in the size range of 200-500 nm*

a./ The synthesis of the ZnO particles was carried out with some modified versions of the same basic process. The two step reaction way [Seelig, Mater. Chem. Phys, 2003] resulted in bidispersed particles. The original one step method [Jezequel, Mat. Sci. Forum, 1994] was realized in a closed autoclave, the resulting dispersion contained polydispersed particles in the size range of 0.5-2 µm. The one step method with atmospherical pressure over the reaction mixture lead to the formation of the monodispersed ZnO particles in the size range of 200-500 nm with very narrow size-distribution (standard deviation <5%).

b./ The formation of the particles follows an aggregation type growth mechanism (as demonstrated in TEM and SEM images), which means that the particles are composed of a huge number of cristalline primary subunits. Considering the growth mechanism remarkable particle porosity was expected. The surface area and porosity of the particles was quantitatively studied by means of N_2 adsorption – desorption measuements and small angle X-ray scattering (SAXS) thechnique. The surface area (a^s_{BET}) was in the range of 50-70 m^2/g, the average pore diameter determined form the hysteresis between the adsorption and desorption curves was between 3 and 4 nm for all samples. The calculated particle density (3.3-3.9 g/cm^3) and porosity (30-40%) can be explained with the voids between the primary crystallites. The SAXS surface area values are significantly higher than the resuts of surface area from the gas adsorption measurements. The reason is that particles contain closed pores which are not accessible for nitrogen molecules. X-ray diffraction measurements revealed the presence of wurtzit crystals of ZnO. The size of the primary crystallites is between 9 and 15 nm depending on the sample.

T6. *Structure and order in Langmuir-films of ZnO particles with average size in the range of 200-500 nm*

The surface pressure vs. surface area isotherms of spread monolayers showed that particles form stable films at the air/water interface, there is no strong cohesivity between the particles. The calculated and the measured contact cross sectional area of a single particle are in good agreement, which reveals that the particles are stable confined in the interface and a compact and hexagonally close packed order was formed during compression.

T7. *Optical properties of single and multilayered Langmuir-Blodgett films of ZnO particles with average size in the range of 200-500 nm*

a./ The UV-Vis reflectance spectra of 1-5 layered Langmuir-Blodgett films of ZnO particles (234±11 nm) were fitted by means of model calculations (Fig.4.). The optical model developed in our group was improved to describe the spectial features of the hexagonally close packed films of monodispersed spherical particles. The model gives good results with single and double layered films in a wide range of the wavelength, for higher layer nubmers the fitting is good in a narrower range. The film thickness and effective refractive index values obtained from the fitting show that the particles sit in the deeper parts between the particles of the former layers. This leads to smaller film thickness compared to the estimated value, namely the diameter of one particle multiplied by the layer number.

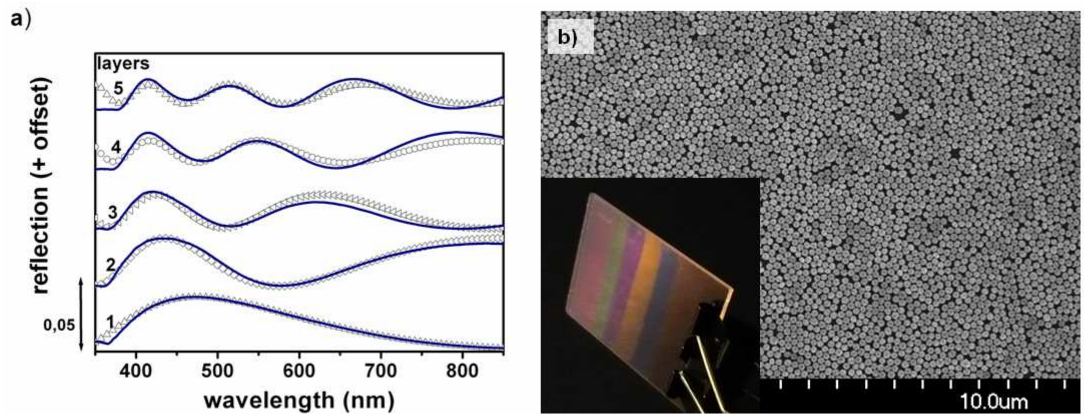

Fig. 4. a) Measured (line) and calculated (symbols) reflectance spectra of 234±11 nm nm ZnO particles. b) SEM image of the single layered Langmuir-Blodgett film, the inserted photograph shows the different colours of the 1-5 layered films in reflection.

b./ The transmittance spectra of the single layered Langmuir-Blodgett films of 301±12 , 349±14 and 457±16 nm sized ZnO particles exhibit the photonic band gap, which is characteristic for ordered photonic crystals. The effective refrective index of the films can be determined based on the position of the first and second order photonic band gaps. The resulting values are significantly higher than the results from the optical model of reflectance measurements, which can be due to the different calculation method for the refractive index. Further calculations make possible to estimate the average particle-particle distances in the films, the result are in good agreement with the expectations based on the SEM images.

c./ Photoluminescence measurements of the quartz supported fims showed a weaker UV emission (390 nm) and a strong, wide visible emission (564-575 nm). The position of the visible emission is determined by the primary crystallite size of the spheres. Increasing primary crystallite size results in red shift of the emission, which can be explained with the size-quantized effects. These results are in good agreement with the observation for the 3-7 nm sized ZnO particles.

T8. *Optimization of patterned particle assembly with ZnO (341±15 nm)*

I have shown that during the particle assembly there are several parameters which must be simultaneously optimized: the surface properties of the particles, the template and the substrate, the stability and the concentration of the particles in the aqueous dispersion and the periodicity of the wrinkled surface of the template. The following parameters lead to the best order of the particles: unmodified particles freshly transfered into water, substrate coated with low molecular weight polyethyleneimine (PEI, MW: 800) and 2-2.5 µm periodicity of hydrophobic template surface. Beside quartz and glass substrates Au coated substrates were succesfully used for particle assembly. SEM images show that the ZnO patterns are composed of multiparticle wide stripes, but particles are not highly ordered in their lines (Fig. 5.).

T9. *Determination of the periodicity of the pattern, photoluminescence emission properties*

The periodicity (wavelength) of the patterns was estimated with two different methods: SEM images and laser diffraction experiments (Fig. 5.). The results were in good agreement, depending on the sample 2.2 - 2.4 µm periodicity was obtained. Laser diffraction measurements provide an easy and fast method for the characterization of the homogenity of the surface: gradient inhomogenity was demonstrated which originates from the PDMS template. The template inhomogenity may be the result of the inhomogeneous distribution of the stress during the wrinkling process.

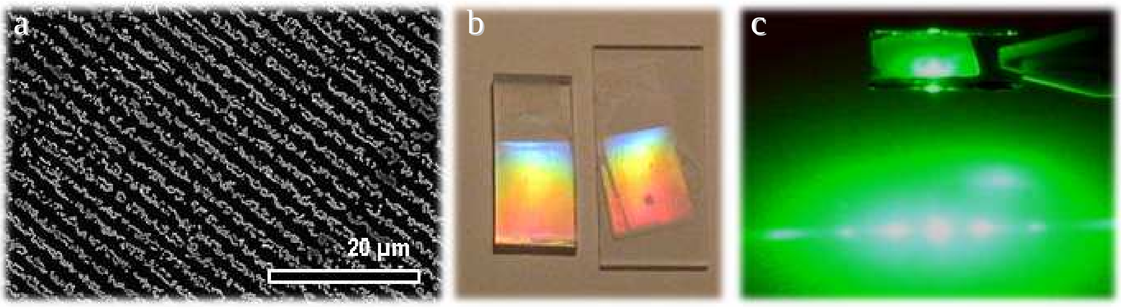

Fig. 5. a) SEM image of the patterned ZnO particles. b) Digital camera image of the patterned surface and the template showing the same diffraction colour. c) Diffraction of laser light on the patterned assemblies.

Photoluminescence emission spectra of the patterned surface exhibit both the UV (383 nm) and the visible (568 nm) emission. Au coated substrates were also used for the emission measurements, the visible emission is shifted towards the higher wavelengths ($\Delta\lambda$=11 nm) and 2-fold enhancement was also observed due to plasmonic interaction: metal enhanced fluorescence is responsible for these changes. Beside the change in the visible emision, the characteristics of the UV emission remained almost unchanged.

Scientific publications

Publications related to the dissertation:

1. **N. Ábrahám**, I. Dékány
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3. **N. Ábrahám**, I. Dékány:
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J. Phys Chem C, 116 (29), pp 15667–15674.

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Összesített hatástényező: 16,756

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2. **N. Ábrahám**, E. Csapó, I. Dékány: Langmuir monolayer study of the interaction of biofunctionalized gold nanoparticles with model phospholipid membranes. 5th Szeged International Workshop on Advances in Nanoscience (SIWAN) 24th-27th October 2012, Szeged, Hungary, Abstr. O28

3. **N. Ábrahám**, E. Csapó, I. Dékány: Interaction of biofunctionalized gold nanoparticles with model lipid membranes, AMSALS2012 Conference, Siófok, Hungary, 3rd-6th June 2012. Abstr. OC49

4. **N. Ábrahám**, I. Dékány: Enhanced photoluminescence of ZnO films on gold coated glass by plasmonic coupling, 25th ECIS Conference, Berlin, Germany, 4th-9th September 2011, Abstr. 430.

5. L. Naszályi és **N. Ábrahám** (joint lecture), A. Ayral, Z. Hórvölgyi: Stabilized Langmuir-Blodgett films of nanoparticles for photocatalytic application, 2nd European COST 540 WG1 Seminar, Toulouse, 2007

Conference posters:

6. **N. Ábrahám**, E. Csapó, I. Dékány: Interaction of biofunctionalized gold nanoparticles with model lipid membranes, AMSALS2012 Conference, Siófok, Hungary, 3rd-6th June 2012. Abstr. P31

7. **N. Ábrahám**, D. Sebők, S. Papp, L. Kőrösi and I. Dékány: Preparation and investigation of monodisperse ZnO particles and their Langmuir-Blodgett films, EuroNanoForum 2011, Budapest, Hungary, 30th May - 1st June 2011, Abstr 306

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