RESEARCH INFRASTRUCTURE NANOENVICZ - NANOMATERIALS AND NANOTECHNOLOGIES FOR ENVIRONMENT PROTECTION AND SUSTAINABLE FUTURE

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The research infrastructure NanoEnviCz integrates Czech scientific institutions and universities renowned for complex interdisciplinary research into broad range of nanomaterials and nanotechnologies. The activity of the RI is focused on the research in the field of nanomaterials, surfaces and nanocomposites for environmental and related applications including 1) the controllable syntheses; 2) complex chemical, structural, morphological and surface characterization; 3) tuning their functional properties; 4) monitoring their potential toxicity and hazard; 5) developing their application in advanced technologies. The RI forms an efficient multipurpose platform both for the partners of the project as well as for the external users from academia, industry, and government organizations. The RI is designed as a platform providing complete services in the R&D and opening access to the unique equipment and the state of the art methodology for users both from academia and industry, inevitable for the accomplishment of priorities of the national strategies of support to R&D&I and for the competitiveness of the Czech science. The research service offered by University J.E. Purkyné under the project NanoEnviCz in the field nanomaterials and nanotechnology summarized as follows:

- Plasma deposition of nanolayers, nanoparticles and nanofilms (metal oxides, polymeric materials, composites) using plasma reactors in various configurations including fluid-bed reactor for plasma treatment of powders;
- Combination of plasma and chemical method for functionalization of surfaces (for catalytic, photocatalytic and sensoric applications and for tissue engineering);
- Characterization of thin films and surfaces – electrokinetic measurements, zeta potential, XPS spectroscopy for surface chemistry;
- Synthesis of nanoparticles (metal oxides and mixed oxides, doped and modifies metal oxides nanoparticles) usable as photocatalysts and reactive sorbents for degradation of highly toxic pollutants including nerve gases, pesticides, cytostatics etc…
- Synthesis of dendrimeric nanostructures for medical applications - drug carriers and biosensing media;
- Development of biosensors for fast and cheap analysis of body fluids - detection of tumor cells.
- Characterization and testing of polymeric nanofibrous materials
- Microbiological laboratory – test of antibacterial activity a cell adhesion for tissue engineering
- Complex analytical laboratory for environmental applications

For more details see: www.NanoEnviCz.cz

STRUCTURE ANALYSIS OF ANTIBACTERIAL FILTRATION MEDIA

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Polymer nanofibers are used in wide range of activities in everyday life, such as: filtration [1], protective closing, pharmaceuticals [2], etc. Due to very small size of pores, these nanofiber in the form of nanotextile are widely used as nanofilters [3]. These nanofilters can capture bacteria [4] and also some kind of viruses [5].

The most versatile method for nanofiber preparation is electrospinning. The industrial application of electrospinning is Nanospider technology, which can produce nanotextiles in high amounts.

We have studied two representatives of polymers (nylon 6, polyvinylidene fluoride (PVDF)) which are used as nanofilters. By one step synthesis we have prepared antibacterial nanofilters by adding antibacterial agents to the solution for electrospinning. We have chosen chlorhexidine (CHX), 1-dodecyltrimethylammonium bromide (DTAB) and benzyltrimethylammonium bromide (BTAB) for modification of nylon 6, and only DTAB for modification of PVDF. We focused our research on structure determination of pristine nanotextiles and on structural changes after the modification by antibacterial agents. We have also
studied surface chemistry of the samples, antibacterial properties and with the help of molecular modeling the interactions between polymer and the antibacterial agent.

Nylon 6
Structure of nylon 6 polymer is very well known. It was resolved that nylon 6 is polymorphic and has two crystal structures: alpha form which was described by Brill [6] and Holmes [7] and gamma form which was determined by Holmes [7]. Both structures are monoclinic and differ from each other by density and arrangement of polymeric chains.

It is known that the electrospinning preparation of nylon 6 nanofibers leads to three structural phases: alpha, gamma and amorphous phase of nylon 6. The dependence of nylon 6 structure on the Nanospider arrangement was investigated. It has been determined, that the phase composition of nylon 6 nanofibers (i.e. the content of alpha, gamma and amorphous phase) depends on electrode distance. In our previous work the core-shell structure model has been suggested, based on combination of XRD and XPS measurements [8]. The fibers exhibit also very strong texture in direction (010).

After the modification by antibacterial agents, there has been significant change of the phase composition of nylon 6 in the case of modification by CHX and BTAB. The rep-

<table>
<thead>
<tr>
<th>Sample</th>
<th>α phase [wt. %]</th>
<th>γ phase [wt. %]</th>
</tr>
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<tbody>
<tr>
<td>PA6</td>
<td>64 ± 5</td>
<td>36 ± 5</td>
</tr>
<tr>
<td>PA6/DTAB</td>
<td>67 ± 5</td>
<td>33 ± 5</td>
</tr>
<tr>
<td>PA6/BTAB</td>
<td>54 ± 5</td>
<td>46 ± 5</td>
</tr>
<tr>
<td>PA6/CHX</td>
<td>54 ± 5</td>
<td>46 ± 5</td>
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**Figure 1.** Diffraction profile for pure PA6 (top) and for modified PA6/CHX (bottom). Calculated profiles for α phase of PA6 (green) and γ phase of PA6 (red) are shown.

**Table 1:** Phase composition of investigated samples.

**Figure 2.** XRD diagrams of powder and nanotextile PVDF.
NANOPARTICLES GROWTH AND ORDERING – SAXS VIEW

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Semiconducting metal sulphide (MS) nanoparticles (NPs) and their superlattices are in the focus of numerous researcher groups since years. These NPs are relatively easy to prepare and exhibit interesting size-dependent electrical, optical, and chemical properties which make them attractive for various applications [1]. They are used in sensor, biomedicine, and optoelectronic applications. Particulary, MS NPs can be used to enhance the energy conversion in organic solar cells [2]. Control over the NPs size uniformity, their shape, and decoration by organic ligand shell is important for their effective employment.
Further enhancement and scaling up of the NPs properties can be achieved by their assembly into superlattices. Of particular importance is the question whether NPs assemble randomly with respect to their atomic planes or along a certain direction of the atomic lattice, and what facilitates such iso-orientated attachment. Superlattices consisting of iso-oriented, single-crystalline NPs, so called mesocrystals [3], have potential for applications as photonic crystals, magnetic storage media, and in technical devices where large stiffness in combination with high elasticity is desired.

In the talk, we report on two X-ray small angle scattering (SAXS) studies of NPs formation [4] and NPs ordering into mesocrystals [5], respectively. In the first study, we applied transmission SAXS in real-time during growth of ZnS NPs. The NPs were formed by reaction of zinc chloride with elemental sulphur dissolved in oleylamine at temperatures 170 °C and 215 °C, respectively. We have simulated the time-dependent SAXS profiles by a model considering spherical ZnS NPs core decorated by organized shell of oleylamine molecules, i.e. core shell particles, which interact via the sticky hard-sphere potential. The SAXS analysis allowed for characterizing influence of temperature, reaction time, and sulphur concentration on NPs structure. In the second study, we use grazing incidence SAXS (GISAXS) to investigate ordering of PbS nano-crystals functionalized with oleic acid in mesocrystals. The mesocrystals were prepared by drying from hexane dispersion of NPs (0.5 mg/mL) on electron microscopy grids and Si 001 substrates. In both studies, the SAXS analysis is combined with X-ray diffraction characterization, to study the metal sulfide lattice of NPs core, and electron microscopy techniques to obtain microscopic images of NPs and their ordering. Additionally, for PbS mesocrystals, selected area electron diffraction (SAED) is used to get insight into alignment of lattice of PbS nano-crystals with the NPs super-lattice orientation.

For the ZnS NPs, the real-time in situ SAXS measurements reveal that the initial nucleation of the NPs occurs in reversed micelles, which disappear when the NPs start to grow. After a rapid initial growth phase, the NPs’ growth slows down after about 30 min of the reaction. Higher reaction temperature or higher sulphur concentration leads to larger nanoparticles and stronger attractive potential between them. By changing the molar ratio of sulphur to zinc salt from one to five in the initial solution, the particle size increases from 2.4 to 3.9 nm. An organized oleylamine ligand shell appears around NPs after their size exceeds certain critical diameter which is around 2.8 nm. The thickness of the shell is about 2.6 nm which matches well with the length of an oleylamine molecule. The polydispersity of NPs is around 30 % and it is independent on the employed reaction conditions.

For the mesocrystals formed of PbS nano-crystals functionalized with oleic acid, we observe body-centered tetragonal (BCT) superlattice of cuboctahedral NPs. The lattice parameters of the BCT NPs superlattice are \( a = b = 10.7 \text{ nm} \) and \( c = 12.8 \text{ nm} \) for NPs average diameter of 6.3 nm. The NPs superlattices are oriented with \([011]_{\text{SL}}\) and \([001]_{\text{SL}}\) zone axes parallel to the sample surface normal for thinner (i.e., few NPs layers) and thicker NPs films. By comparing scanning transmission electron microscopy images of the superlattice and the SAED of the nano-crystals’ PbS lattices we conclude that the PbS lattice planes \(\{100\}_{\text{PbS}}\) are parallel to the \(\{100\}_{\text{SL}}\) planes of the NPs superlattice. At the same time, the PbS nano-crystals are oriented with \([011]_{\text{PbS}}\) zone axis parallel to the sample normal, i.e. parallel to the \([011]_{\text{SL}}\) superlattice zone axis for thinner films. We explain formation of the BCT lattice and the alignment of the nano-crystal lattice with the superlattice of the NPs by favourable mutual interaction of nano-crystals’ facets covered with ligand where forces between neighbouring \(\{100\}_{\text{PbS}}\) -\(\{100\}_{\text{PbS}}\) and \(\{111\}_{\text{PbS}}\) facets are balanced.

In both studies, SAXS has crucial role for characterization of NPs and their superlattices and the employment of the scattering technique for these kind of material systems will be highlighted in the talk.