EMERITUS GROUP

Nanostructured Interfaces

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The department Interfaces has been terminated with my retirement on 31 January 2014, and the group leaders on permanent positions, G. Brezesinski, R. Miller and H. Riegler were transferred to the departments Colloid Chemistry, Biomaterials and Theory & Bio-Systems, respectively. Their report is thus integrated into that of their department. Also E.V. Skorb has moved to the department Biomaterials, and she is reporting there as independent postdoc. Therefore this report focusses on work, where I as emeritus have been involved. This concerned continuation of work of the previous groups of A. G. Skirtach and D. G. Shchukin, who have left on professor positions, but where some scientists were completing their work in collaboration with these former group leaders before they found the next position. In addition there were independent postdocs who were directly supervised by me, and I also continued cooperation with former co-workers, where the experiments were performed at their new positions.

As the topics are rather diverse, resulting in about 60 publications in the reporting period, this report concentrates on only few highlights intended to show the breadth:

Feedback Active Coatings

This subject concerns a long development predominantly to achieve corrosion protection. There corrosion inhibitors are incorporated into nano- or microcapsules that release their cargo upon an environmental stimulus. This may result from a defect in the material to be protected, e.g. a change in pH or redox potential **(Fig. 1).** The process has been shown to work in many cases, and the research concerns the development of different types of containers **[1].** The types of containers, that have been studied, varied from polyelectrolyte multilayer capsules to hollow silica nanotubes (halloysites) to mesoporous inorganic containers. As a recent achievement it could be shown for porous silica containers that with the same amount of inhibitor loaded smaller capsules (80nm diameter) provide a much better corrosion protection than large ones (diameter 700 nm).This is demonstrated not only by macroscopic scratch tests, but also by impedance spectroscopy and by the scanning vibration electrode technique allowing a local resolution **[2].** Work under this topic develops more and more into very concrete applications and for this funding has been achieved from the federal ministry of economy with the aim to found a start-up company. The main problems in commercialization are not the corrosion protection or missing economic benefits, but side reactions with the container material, leading to smell. In any case the ecologic benefits are obvious, as the cancerogeneous Cr (VI) can be avoided as protective agent.

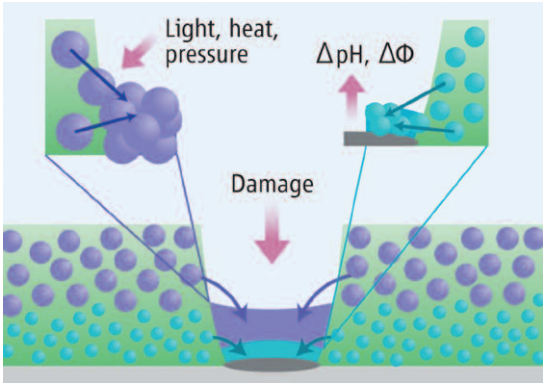

Fig. 1: Nanocontainer-based smart coatings. A fine dispersion of nanocapsules lends active functionality to the coating matrix. Capsules (spheres) can be loaded with various active materials depending on the functionalities required. The sensitivity of the capsule shell can be adjusted to different stimuli (e.g. pH changes or changes in the electrochemical potential) for opening and release of the encapsulated active material by nanoengineering of the shell components and structure. ***[1]***

Manipulation and Study of Membranes and Cells by Nanoplasmonics

In cooperation with University Gent and Jacobs University Bremen cells were manipulated by optically exciting metallic nanoparticles and nanorods. If these are attached to a membrane, the membrane can be reversibly opened to transient currents. These single channel currents can be studied by means of supported bilayer membranes **(Fig. 2) [3].**

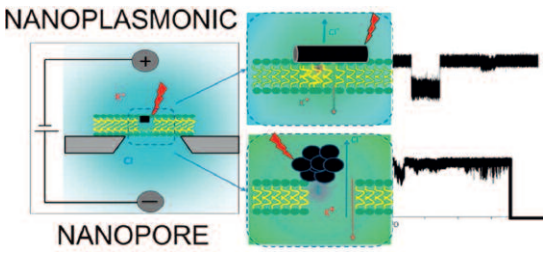

Fig. 2: Left: Schematics of a set- up to measure the conductance of a single channel in a membrane. Middle: Sketch of a nanorod or a nanoparticle aggregate with strong IR absorption to create local heating by light. Right: Single channel conductance/time traces. ***[3]***

Engineering of Nanoparticle Surfaces for Optimized Raman Detection

Huge efforts have been devoted to arrive at an ultrasensitive detection of Raman signals from the interior of different cells. These efforts basically involve the design of so-called hot spots, i.e. local spaces with extremely high intensity of the electromagnetic field. These exist at sharp tips of metallic nanostructures, most intensely at the junction of two or more tips. At these junctions the tips should be as close as possible, but at sufficient distance to leave space for the analyte. The main challenge is to establish these structures with high precision and reproducibly to arrive at a quantitative signal enhancement. An example of such a structure is given in **Fig. 3.**

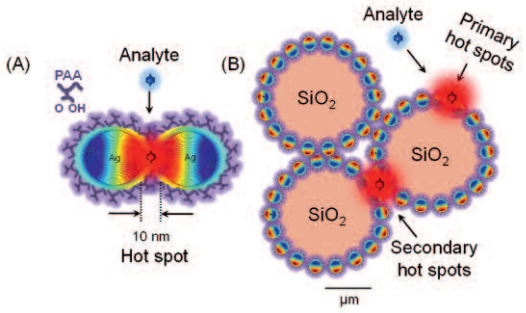

Fig. 3: Schematic illustration of primary and secondary SERS hot spot formation by Ag-PAA (polyacrylic acid) nanofilms on colloidal silica. (A) Pre-formed silver nanoparticles are embedded in the matrix of PAA (Ag-PAA nanofilms) with fixed gaps (~10 nm) that can serve as primary SERS hot spots. (B) Ag-PAA nanofilms are deposited on silica microparticles (~1.5 µm) that can form secondary SERS hot spots at the interparticle junctions during self-assembly. ***[4]***

Ag nanoparticles are coated by a thin polymer film that enables penetration of low molecular weight compounds, but keeps the nanoparticles apart. These nanoparticles are adsorbed on the surface of S_iO_2 microparticles, and at the junction of 2 such microparticles a hot spot with reproducible dimension can be established. This hierarchical structure is still smaller than a cellular dimension and thus can be brought into a cell for imaging or sensitive local analysis of cellular compartments. An example on this is given in **Fig. 4 [4].** Obviously one can create images using the most pronounced lines in the spectra that correspond to nucleus, cytoplasm, etc., but above all the information content is so rich that it has not yet been analyzed in more detail. At this stage these studies concern first principles laying the ground by additional calculations of local field strength. Theory and experiments agree that enhancement factors around 10^9 can be achieved, and this suffices also for single molecule detection.

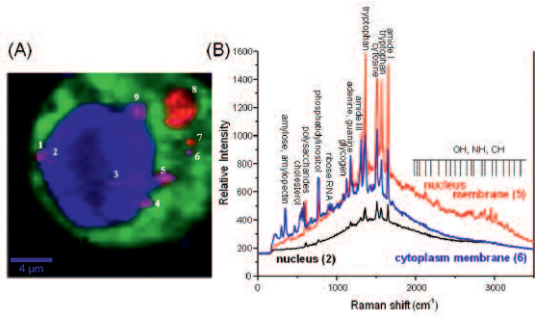

Fig. 4: (A) Raman spectroscopic imaging of a live NIH/3T3 fibroblast with embedded SiO_2@Ag-PAA particles in a colored spectral map (scale bar is 4 µm). The map reflects the differences found in the Raman data and SERS active Ag-PAA nanofilms. This map is a linear combination of the averaged single spectra and characteristic for cell compartments (green cytoplasm and blue – nucleus). Intense green and blue colors of spots separated by a darker background contrast indicate the presence of SERS effective SiO_2@Ag-PAA particles inside the cellular medium. Spots with violet and red colors show SiO_2@Ag-PAA particles that are located at the membrane interface or at its surface (highlighted with numbers). A confocal Raman image is generated by integration of the intensity of the strongest bands in the three spectral ranges: (i) <1000 cm^{-1}, (ii) 1000-2000 cm^{-1} and (iii) 2500-3500 cm^{-1} after local baseline subtraction using the hypercluster analysis (HCA) as one of the efficient label-free methods for the visualization of intracellular components and processes. (B) Selected SERS spectra that are collected from nucleus (2 in A) and periphery membranes of the nucleus (5 in A) or cytoplasm (6 in A). The laser excitation wavelength was 532 nm and the grating was 600 g mm^{-1} (BLZ = 500 nm) and spectral resolution of 3 cm^{-1}. ***[4]***

A similar approach decorating S_iO_2 microparticles with carbon nanotubes and Au nanoparticles also led to well resolved cellular Raman images, but in this case theory and the approach are not yet as well developed **[5].**

References

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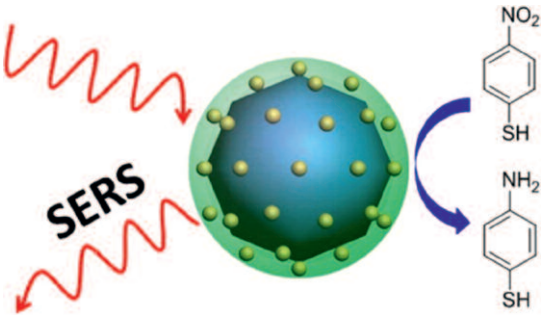
[8] Pinchasik, B.E., Möhwald, H., Skirtach, A.G.: Mimicking Bubble Use in Nature: Propulsion of Janus Particles due to Hydrophobic-Hydrophilic Interactions. Small **10,** 2670-2677 (2014).

Surface Enhanced Raman Spectroscopy and Catalysis

Au nanostructures are well established catalysts. Therefore these nanostructures can be used not only for catalysis, but at the same time the high sensitivity can also be used for studying reaction intermediates **(Fig. 5).** This has been achieved using a model reaction in cooperation with Univ. Potsdam and Beijing Univ. of Science and Technology **[6].**

Fig. 5: A Au „nanoflower" (blue core) with high specific surface is coated with a gelatin film in which catalytitically active Au nanoparticles were synthesized in situ. A catalytic model reaction can then be followed by surface enhanced Raman spectroscopy (SERS). ***[6]***



Nanoplasmonic Surfaces

The development of colloidal lithography was extended and cultivated at Jilin University to obtain films with unusual optical as well as wetting properties. With this technique one first prepares an organized layer of latex spheres, that then are etched into a cone by reactive ion etching **(Fig.6).**

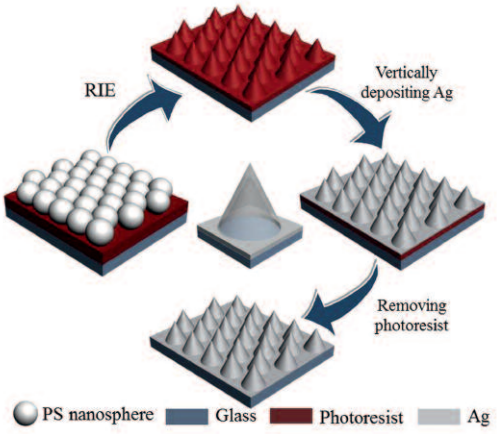


Fig. 6: Outline of the process for fabricating hollow nanocone array films. The central schematic shows a transparent hollow nanocone to stress the relevance of the central structural element. ***[7]***

Coating the structure with Ag and removing the organic part then leads to arrays of Ag cones. Varying the etching angle one may also produce asymmetric cones or cones with the tip truncated (volcanos). This then results in structures with unusual properties. As example **Fig. 7** shows that a Ag film with a thickness of about 100 nm is intransparent, but a film of cones with the same Ag thickness is reasonably transparent. By means of field simulations one can understand this as an interaction of a surface plasmon at the base and at the tip of the cone **[7].**

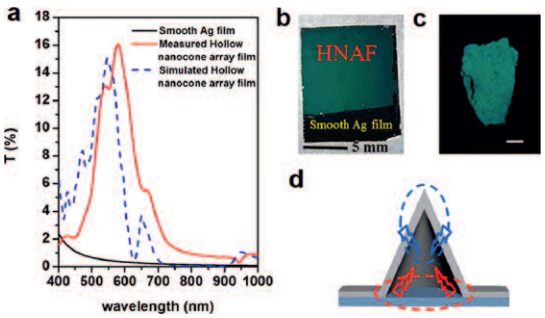


Fig. 7: (a) Measured (red curve) and simulated (blue dash curve) transmission spectra of a hollow nanocone array film (HNAF) and a 100 nm Ag film with the same thickness (black curve). (b) Optical image of an HNAF sample with a small part of a smooth Ag film at the bottom. (c) Optical image of a HNAF island surrounded by a 100 nm smooth Ag film. The scale bar corresponds to 10 µm. (d) Description of one single unit of the hollow nanocone array and the predicted mechanism generating the greatly enhanced optical transmission. ***[7]***

Self-Propelling Janus Particles

A method has been developed to prepare Janus particles, i.e. particles with 2 different sides. One side is coated with catalytically active Ag nanoparticles, where a gas is created **(Fig. 8).** This bubble preferably grows on hydrophobic areas and its formation causes directed motion. Near a surface the nanoparticle/bubble couple may be attracted or repelled from the surface, and therefore via changing the hydrophilicity of the surface one can switch between surface and bulk motion **[8].**

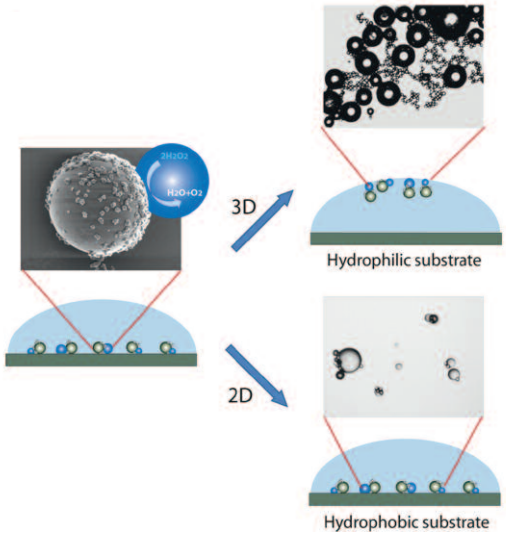


Fig. 8: Janus particles propelled by the formation of an oxygen bubble due to the splitting of H_2O_2. Increased hydrophobicity of the glass substrate changes the particle motion from three- to two-dimensional. ***[8]***

Functionalized Fullerenes as Amphiphiles

Previous work in the joint laboratory with the National Institute of Materials Science in Tsukuba was based on the notion that aromatic and aliphatic systems are incompatible. Hence fullerenes with aliphatic chains attached can behave like amphiphiles, but not in water. Thus they form organized structures in organic solvents like traditional amphiphiles in water (bilayers, micelles) **[9].** Technologically this is interesting, as one phase contains a high concentration of pi-electrons, which are responsible for high charge carrier mobility and special optical properties. This work has meanwhile been extended to demonstrate the existence of even worm-like micelles **(Fig. 9) [10].**

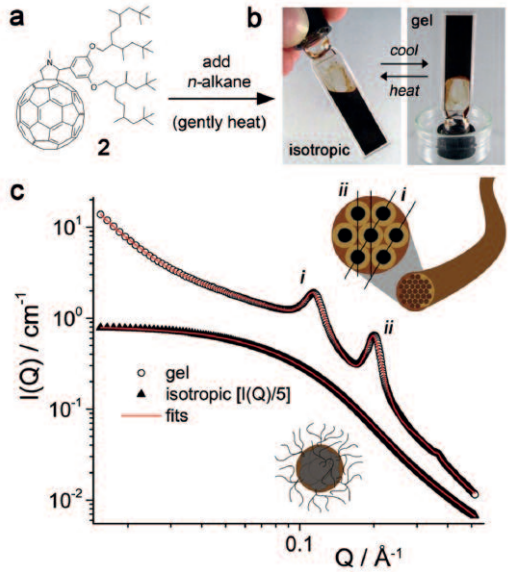


Fig. 9: Gel formation by ***2,*** *driven by addition of n-alkane solvents. a) Chemical structure of* ***2.*** *b) Photographs showing the gelled and isotropic states that arise on dissolving 2 in n-decane. c) Fitted synchrotron SAXS data for 2 with n-hexane, 2 at 19.8 wt%, taken at 5°C (gel state) and 55°C (isotropic state), respectively. Red lines indicate fits to the data. For clarity, the SAXS data and fit for the isotropic state have been divided by a factor of 5. Inset: schematic depictions of the structures (micelles and gel fibres) present in the system in both states. The peaks in the SAXS data taken at 5°C marked i and ii arise from a hexagonal arrangement of the C_{60}-rich columns within the fibres, with d-spacings corresponding to the distances indicated on the schematic of the gel fibre. The steep increase in I (Q) at low Q suggests a fractal-like network structure, indicating that individual fibres are bundled and substantially interwoven.* ***[10]***

Self-assembly of Peptidic Structures

There exist known peptide libraries that endow these systems self-assembly. This could be used to form tubes that possess wave guiding properties as well as capsules with responsive properties. These systems are further continued in cooperation with the Chinese Academy of Science Institutes of Chemistry and Process Engineering **[11].** They exhibit the special property that the structure depends sensitively on environment.

Final Remark

The work of the emeritus group has been experimentally terminated in Golm, with the exception of the work on self-repairing coatings, but is continued at various external institutions, to a large part in cooperation with our institute. I received recently as awards from the ACS the Langmuir lectureship and the Elhuyar-Goldschmidt award from the Royal Spanish Society of Chemistry. I am grateful for this, but especially for the many co-workers, who contributed much to our success and who now can continue their career in our institute or at other institutions in the world.

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