EMERITUS GROUP

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Nanostructured Interfaces and Composites General

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The Emeritus group was working until 31.01.2016, and after that time I have been as guest in the institute without responsibility for people and laboratories. The main aim has been to finish work started in the department interfaces and to transfer projects to other institutions and help scientists advance their career. Hence I have continued mentoring various young scientists in the MPICI or worldwide, mostly but not exclusively former co-workers. This involved discussions and advices on a personal as well as scientific level, and concerning the latter the interaction has often been so close, that it yielded joint publications. Some of the joint work will be listed below.

Experimental Work in the MPICI

The group had a long-lasting effort to transfer knowledge gained on self-repairing coatings into applications. It is based on corrosion inhibitor filled containers releasing their content upon an environmental change in pH or redox potential, typical for a corrosion pit. The technical feasibility had been demonstrated and patented by the Max Planck Society. The economic and ecologic advantages had also been elaborated. Scientifically appealing remained the development of new containers by different methods, and one approach is emulsion polymerization. In this case one can prepare core/shell particles by polymerization in an emulsion droplet, if the polymer is insoluble in the oil and precipitates to the droplet surface. We already in 2012 introduced an approach established in other fields, where the oils as well as the polymers are characterized by the so-called three Hansen parameters. These describe polar, dispersion and hydrogen bonding interactions. By systematic studies of polymer swelling in different solvents we could then show for different polymers, how different the parameters of oil and polymer can be still to enable solubility. Thus we derived solvent conditions to obtain compact, core/shell or multicompartment capsules **[1].** (**Fig. 1**)

This project has been transferred to a cooperation partner (Enviral), and discussions are ongoing, if they would license and produce coatings in the company or if a start-up would be founded with participation of the Max Planck Society.

Work on sonochemical modification of solids and light induced pH changes to manipulate responsive hydrogels by the groups of E. V. Skorb (now Harvard Univ., Boston) and D. V. Andreeva (Uni Bayreuth, now Institute for Basic Research, Ulsan, Korea) will be reported in the chapter of the Biomaterials department, where these experiments have been perfomed with my participation.

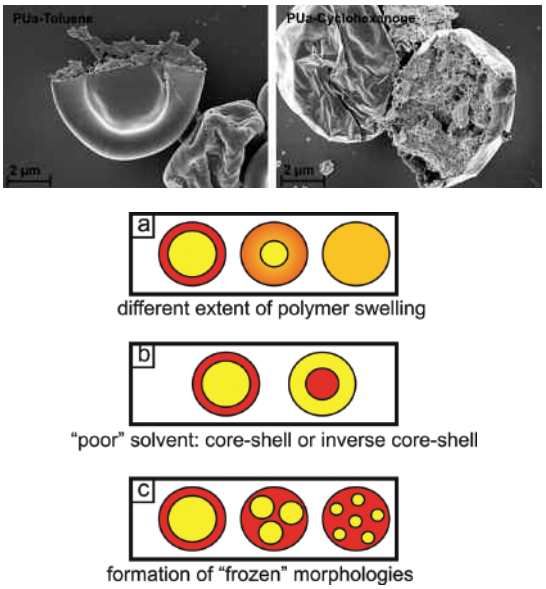

Fig. 1: Left: Electron microscopic images of capsules with core/shell (top) or with compact morphology (bottom) depending on the solvent toluene or cyclohexanone, respectively. Right: Scenarios of different morphologies depending on the solvent quality. ***[1]***

Experimental Work Outside the MPICI

Nanoplasmonic Surfaces

The most intense cooperation has been with the group of G. Zhang at Jilin University **[2].** There the technique of colloidal lithography in connection with angle dependent reactive ion etching has been extensively refined to obtain extremely regular nanostructured Ag surfaces. As an example **Fig. 2A** shows Ag nanocone arrays, which in this case serve to trap light at specific wavelengths, depending on the structure, that can be manipulated by the preparation conditions. Consequently the intensity of the surface enhanced Raman spectrum (SERS) strongly depends on the excitation wavelength (**Fig. 2B**). The trapping of light near the cone foot can be also simulated by finite difference time domain (FDTD) simulations for different cone heights as shown **in Fig. 2 C-F.**

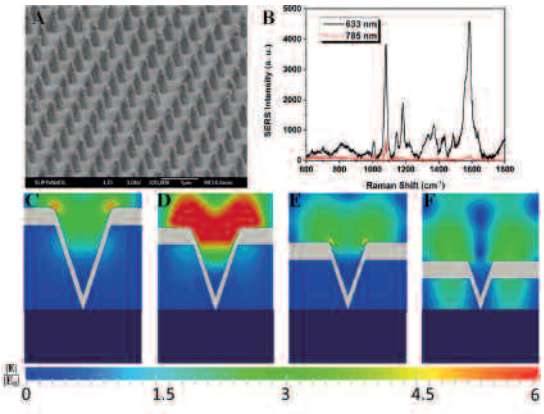

Fig. 2: A: Electron micrograph of an inverse Ag nanocone array, B:SERS spectra of p-aminothiophenol in these arrays for two different wavelegths, C-E: simulated electric field intensities for cone heights of 500, 400, 300 and 200 nm, respectively at the maximum absorption wavelength ***[2]***

As a very new and exciting way of surface structuring we have managed to prepare slits with width controlled to better than 1 nm (**Fig. 3**) by a technique called nanoskyving. Such a structure is sketched in **Fig. 3a,** and the dark lines in the center in b-f indicate, that the gap width can be varied with nm precision. This is important, as the FDTD simulations in **Fig. 3g** reveal, that the highest field strengths are achieved for an intermediate gap width of 5 nm. This can be verified by the SERS spectra of a probe, that exhibit maximum intensity for a 5nm gap width. One also realizes, that there is a periodic field variation along the normal to the macroscopic surface, indicating a three dimensional standing wave in the gap. Hence also the height of the structure, in this case 150nm, is important. **[3]**

These structures are interesting on one hand because of plasmonic effects, on the other hand they enable the study of molecules in well-defined, confined geometry, e.g. polymers with motional constraints. These studies will be continued in cooperation with the department of A. Fery at the Institute of Polymer Research, Dresden.

As another offspring from this research we have started to study photochemistry in the plasmonic field, which indeed shows , that one can deposit a photoproduct, in this case Ag nanoparticles, at positions of maximum plasmonic fields (unpublished).

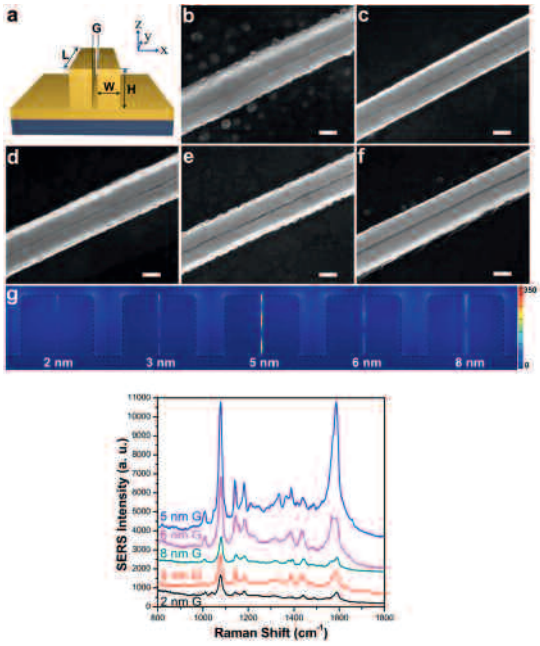

Fig. 3: a) Sketch of a 1D nanogap structure with selectable parameters. b-f) SEM images of Au nanogaps with widths 2, 3, 5, 6 and 8 nm. g) FDTD simulations of the plasmon field intensities in the nanogaps with scale colors representing field intensities (from ref. 3). Bottom: SERS spectra of a dye probe for different gap widths. ***[3]***

Capsules from Peptide Assemblies

In cooperation with the group of Xuehai Yan at the Institute of Process Engineering in Beijing peptide assemblies were studied into different directions:

- They can be responsive and biocompatible drug delivery vehicles.
- They may serve as biomimetic structures directing light to reactive centers, where a product is desired.

In an optimum way light could generate a photocatalyst, that uses the light path previously optimized or self-organized for optimum light capture. For the first case **Fig. 4** presents a scheme of the assembly of a peptide/ porphyrin particle that is intended to serve for photodynamic therapy. The success is also demonstrated in an animal experiment, where the particle administration and light activation demonstrate a decay of the tumor with time **[4].**

References

[1] A. Latnikova, D. Grigoriev, H. Moehwald, D. G. Shchukin: Microgel containers for self-healing polymeric materials: Morphology prediction and mechanism of formation. Polymer, 73 183-194 (2015).

[2] B. Ai, P. Gu, Z.G. Wang, H. Moehwald, L. Wang, G. Zhang: Light Trapping in Plasmonic nanovessels. Adv. Opt. Mater. 5, 16000980 (2017).

[3] Z.W. Zhou, Z.Y. Zhao, Y. Yu, B.Ai, H. Moehwald, R.C. Chiechi, J.K.W. Yang, G. Zhang: From 1D to 3D: Tunable Sub-10 nm Gaps in Large Area Devices. Adv.Mater. 28, 2956-2963 (2016).

[4] K. Liu, R. Xing, Q. Zou, G.H. Ma, H. Moehwald, X.H. Yan: Simple Peptide-Tuned Self-Assembly of Photosensitizers towards Anticancer Photodynamic Therapy. Angew. Chemie 55, 3036-3039 (2016).

[5] K. Liu, RR. Xing, Y.X. Li, Q.L. Zou, H. Moehwald, X.H. Yan: Mimicking Primitive Photobacteria: Sustainable Hydrogen Evolution Based on Peptide-Porphyrin Co-Assemblies with a Self-Mineralized Reaction Center. Angew. Chemie, Int.Ed. 55, 12503-12507 (2016).

[6] D. Radziuk, H. Mohwald: Ultrasonic Mastering of Filter Flow and Antifouling of Renewable Resources. Chem. Phys. Chem.17 931-953 (2016).

[7] R. Boubeki, M. Gross, M. In, O. Diat, M. Nobili, H. Moehwald, A. Stocco: MHz Ultrasound Induced Roughness of Fluid Interfaces. Langmuir 32 10177-10183 (2016).

[8] B. Parahonskiy, M.V. Zyuzin, A. Yashchenok, S. Carregal-Romero, J. Reiman, H. Möhwald, W.J. Parak, A.G. Skirtach: The influence of the size and aspect ratio of anisotropic, porous CaCO3 particles on their uptake by cells. J. Nanobiotechnology 13, 13:53 (2015).

[9] D.X. Ye, Y.Y. Ma, W. Zhao, H.M. Cao, J.L. Kong, H.M. Xiong, H. Möhwald: ZnO-Based Nanoplatforms for Labeling and Treatment of Mouse Tumors without Detectable Toxic Side Effects. ACS Nano, 10 4294-4300 (2016).

[10] S.H. Peng, B.E. Pinchasik, H. Hao, H. Moehwald, X.H. Zhang: Morphological Transformation of Surface Femtodroplets upon Dissolution. J.Phys.Chem.Lett. 8, 584-590 (2017).
[11] Han, X., Hou, J.; Xie, J., Yin, J., Tong, Y., Lu, C.,: Synergism of Dewetting and Self-Wrinkling to Create Two-Dimensional Ordered Arrays of Functional Microspheres. ACS Applied Materials & Interfaces 8 (25), pp. 16404-16411 (2016).
[12] Al-Rehili, S., Fhayli, K., Hammami, M. A., Moosa, B., Patil, S., Zhang, D., Alharbi, O.; Hedhili, M. N.; Möhwald, H.; Khashab, N. M.: Anisotropic Self-Assembly of Organic-Inorganic Hybrid Microtoroids. *Journal of the American Chemical Society.* doi:10.1021/jacs.6b10080 (2016).

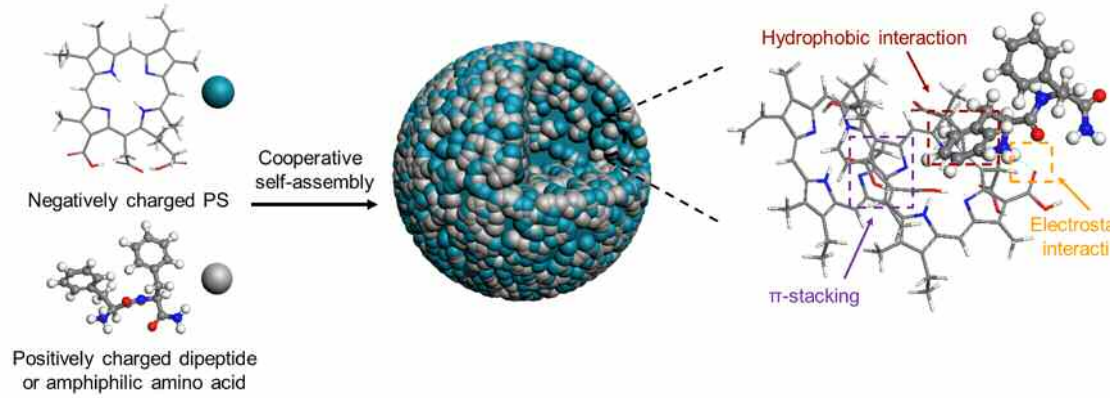

Fig 4: Scheme of the assembly of a nanoparticle from a cationic dipeptide and a porphyrin that serves as sensitizer for photodynamic therapy, d) development of an animal tumor with time after treatment with the free drug (red), with drug/peptide particles (blue) compared to the control (black). ***[4]***

On the second topic, we have shown that self-assembling a porphyrin and a peptide may lead to a tubular structure with strong $\Pi - \Pi$ interactions. This then leads to efficient excitonic energy transfer along the tubes. In the presence of titania and Pt one thus photoproduces TiO_2 and Pt particles, and these may serve for water splitting and hydrogen production, respectively (**Fig. 5**) **[5].** This could be a model of simple prebiotic H_2 producing bacteria resulting from self-organization of molecules and minerals.

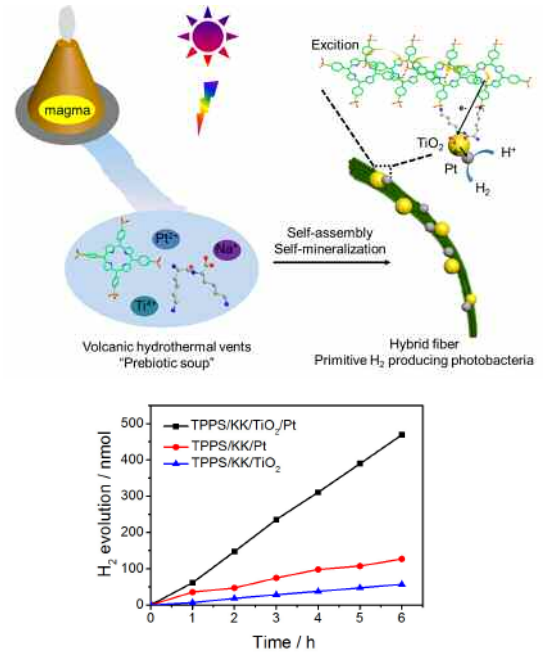

Fig. 5: Left - Scheme of the tubular assembly of a dipeptide and a porphyrin leading to enhanced exciton transport. In the presence of metal ions one then can synthesize nanoparticles, that can catalytically split water (TiO_2) and convert this into hydrogen (Pt). Right: Photoproduced hydrogen for tubules only coated by titania (blue), by Pt (red) and by both nanoparticles (black). ***[5]***

Ultrasonic Enhancement of Phase Transfer

In cooperation with the Institute for Separation Chemistry at Marcoule (T. Zemb) and Univ. Montpellier (A. Stocco) we studied the possibility of enhancement of phase transfer by ultrasound to improve oil/water separation. One effect could be to reduce the clotting of filters /6/, another to roughen the interface by ultrasonic excitation. The latter has been measured by optical reflection and ellipsometry under excitation with MHz ultrasound. **Fig. 6** shows, that roughnesses around 100 nm can be achieved for the oil/water as well as for the air/water interface. **[7]** This is a promising result, but experiments, if this really enhances phase transfer, are still missing.

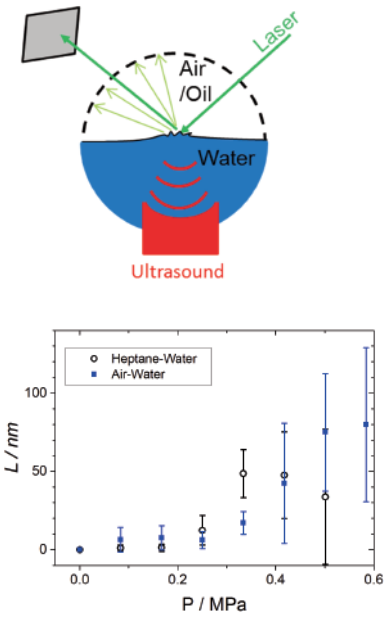

Fig. 6: Left: Scheme of the set-up to measure optically the surface roughness under ultrasonic excitation. Right: Surface Roughness L for different ultrasonic intensities for the air/ water (blue) and for the oil/ water interface (black). ***[7]***

Cooperations with other Groups

As space is limited I would like to mention briefly only a few groups, where the interaction has been most intense and fruitful. In a cooperation over years with the groups of A. G. Skirtach (Univ. Gent) and D. V. Gorin (Univ. Saratov) we studied the penetration of nanoparticles into cells. Together with the groups of A. Yashchenok and B. Parahonskiy we now showed that elongated nanoparticles are easier uptaken, probably because of the stronger adhesion and membrane distortion **[8].**

The group of H. M. Xiong at Fudan Univ. in Shanghai has long-lasting experience in preparing ZnO nanoparticles These are biocompatible, can be made porous and photoluminescent. Therefore we could show that they are very suitable carriers for theranostic applications **[9].**

The group of X. Zhang at the Royal Melbourne Institute of Technology has developed powerful methods to control oil/ water separation in a microfluidic channel, and the precipitation can lead to defined nanodroplets on surfaces. On patterned substrates one can form unique droplet shapes, and their evolution is determined by minimization of the surface energy. These shapes have been simulated in cooperation with B. E. Pinchasik at the MPI of Polymer Research in very good agreement with experiments **[10].**

The group of C.H. Lu at Tianjin Univ. had developed here the technique of periodically wrinkling of a surface by stretching and compression, that can be made very regular on large areas. Now we have extended this in combination with controlled dewetting to obtain regular colloid arrangements on large areas **[11].**

With the group of N. Khachab at the King Abdullah University the anisotropic and chiral interactions of Fe2O3 nanoparticles have been used to achieve unusual assemblies. In special we have achieved toroidal arrangements **[12].**

Outlook

This will be my last contribution to the biannual report of the MPICI, as most of my future work will not be performed in the institute. Besides the activities as associate editor for ACS Nano and consultant for CEA and for Jilin University I will continue mentoring young scientists irrespective if I am co-author of their publications, and some of the related groups have been mentioned in this report. It has been fun working with these, and it has also been fun to work with many highly motivated scientists as well as non-scientists in the institute, and I want to thank them and my colleagues for the friendly and cooperative atmosphere. Above all I would like to thank my former secretary Stefanie Riedel for the many efforts she spent for the department and me. She was the manager of the department as well as of the Emeritus group. She as well as the other co-workers, once given enough freedom, will equally well perform in other environments, and I wish them good luck.

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