# Final report for project Nr. 105173

During the course of the project the main goal was to rely on wet-chemical approaches to create hierarchical assemblies with special properties using colloidal particles. The main results of the project are appropriately documented in high-impact factor international publications (total impact factor ca. 64) and are summarised below. In addition to the regular research articles, a review in Advanced Materials on colloidal interaction governed nanoparticle clusters has been also delivered. The core concept of all the work done within the framework of this project relies on the preparation an investigation of either bulk or interfacial nanostructures. Several young researcher and university students were involved in the project, allowing them to successfully obtain PhD, MSc or BSc degrees:

Dániel Zámbó (PhD ongoing - expected completition: 2016)
Szilárd Pothorszky (MSc, PhD ongoing- expected completition: 2017)
Eszter Gergely-Fülöp (PhD)
Dániel Péter Szekrényes (BSc, MSc ongoing)
Enikő Traply (BSc, MSc ongoing)
László Bicsérdy (MSc)
Gergő Fülöp (BSc, MSc)
Zsuzsanna Molnár (BSc, MSc)
Blanka Mohácsi (BSc, MSc)
Katalin Megyesi (MSc)

## I. PARTICLE ASSEMBLIES

(i) mPEG-SH coated spherical gold nanoparticles have beed synthesised in different sizes. We successfully demonstrated that for this system temperature as a control parameter can be used to initiate assembly of the particles by reducing the range of the steric interaction between the nanoparticles, i.e. triggering the collapse of the polymer coils. Although the LCST of PEG is well outside of the boiling point of water, at high ionic strengths the particles can undergo clustering already around 55 °C. Our detailed DLS and spectroscopic studies can be interpreted by our calculations on the colloidal interactions, that were performed for the specific systems under investigation. Optical simulation of the particle plasmons and the coupled modes and their comparison with the measurement data allowed us to extract the smallest distance between the nanoparticles in the aggregate. There results were published in Langmuir (Zambo et. al. Langmuir 2015)

(ii) The kinetic control over the colloidal interaction governed clustering of mPEG-NH2 coated spherical gold nanoparticles has been studied based on the above mentioned publication. We provide indirect proof, that the collapse of PEG molecules (triggered by temperature increase at high salt concentration) can be tuned continuously, i.e. allowing to fine tuning of the steric repulsion between nanoparticles, resulting in different clustering kinetics. This in turn allows to more closely achieve the theoretically optimum few kT potential energy depth in case of a 'soft-sphere' type interaction, allowing the growth of nanoparticle crystals from identical particles. Our result are summarised in Zámbó et. al. RSC Advances 2016.

(iii) Self-assembly of patchy nanorods and nanospheres: we found the optimised conditions for the tip-selective surface modification of gold nanorods with cysteamine molecules and consequent side-selective PEGylation. We provided solid experimental evidence for the patchy surface chemistry of the nanorods, that allows in theory the site-selective binding of charged spherical nano spheres at the tips of the nanorods. Based on electron microscopy, our main finding is that assembling 19 nm nanospheres with nanorods 54 nm in length the tip selective binding of two nanospheres at the opposite end of the nanorods can be achieved. As the sphere-to-rod size ratio increased, however, first the two bound particles were found to be significantly shifted around the perimeter of the rod's tip. For even larger sphere-to-rod size ratio, only a single sphere is attached at the side of the rods. Electrokinetic and spectroscopic data suggest that the origin of this apparent change of the assembly behaviour is a direct consequence of the inhomogeneous spatial extent and strength of colloidal interactions between the patchy rods and the spheres. The obtained results are summarised in Pothorszky et. al. Nanoscale 2016.

(iv) We submitted recently a manuscript to Nanoscale on the preparation of "mushroom" like Janus particles, which could be used to perform and investigate directed assembly. The Janus particles are composed of gold and silica, where a silica cap only partially covers the gold core.

(v) In a collaborative work with colleagues form the Budapest University of Technology and Economics and Japan, we used our expertise in colloidal interaction design and calculation to investigate the self-assembly of nanoparticles by an autocatalytic front (Bohner et. al. Langmuir 2015) and measured the evolution of a Voronoi pattern due to ionic strength induced nanoparticle aggregation and diffusion of gold nanoparticles in a hydrogel (Zambo et. al. PCCP 2016).

## II. INTERFACIAL NANOSTRUCTURES

### (i) Monolayers of gold nanorod/mesoporous silica core/shell particles

It has been investigated how an asymmetric gold nanorod coated with a thin mesoporous silica shell could act as a platform allowing moieties of certain sizes to reach the gold core particle inside the shell (Fülöp et. al. 2014 MatChemPhys). For this purpose the core/shell particles have been heat treated at 300 °C with transferred them into spherical particles. After this, the particles were subjected to a chemical growth procedure, in which Au(I) reduction relies on the catalytic decomposition of ascorbic acid on the gold particle's surface. The results have shown that the spherical core shell particles can be grown back into rod shaped core/shell particles, indicating three main aspects of the system: a) the ascorbic acid can indeed reach the interior of the core/shell particle by diffusing through the mesopores of the shell (b) the rules applying during the bulk growth of nanorods are also valid for the chemical reaction performed inside the shell and (c) the mesoporous shell is elastic, allowing several cycles of rod-to-sphere-to-rod shape conversion. Due to the growing size of the core particle, however, the process naturally possess an upper limit. To gain a more complete picture about how the temperature treatment affects the shape transformation of the nanorods, a systematic study involving nanorods with different aspect ratio has been carried out as well (Fülöp et al. 2014 PeriodicaPolytechnica).

### (ii) Hybrid layers

Graphene/gold hybrid systems are subject of intensive research due to the potential of graphene's electrical properties and its interaction with plasmonic nanostructures. In cooperation with other colleagues at our institute we provided a well defined system of suspended graphene on gold nanoparticles (Osváth et. al. 2015 Nanoscale), for which first optically inactive particles have been used to study the suspended graphene layer in its own (Osváth et. al. 2014 Nanoscale), showing that the suspended regions of the graphene show a different doping compared to the graphene/nanoparticle junction regions. Scanning tunnelling microscopy, confocal Raman and conventional

Vis spectroscopy measurements indicated Raman scattering of the suspended graphene can be increased due to the plasmonic near-field - graphene interaction, and the samples show interesting optical scattering and reflection properties (Osváth et. al. 2015 Nanoscale).

We also used an interfacial assembled monolayer of silica particles with different sizes (25 nm and 400 nm) as a template layer to grow 70 Angstrom of Fe layer on top of the nanoparticles and follow the evolution of magnetism in the ultrathin, curved iron films. We found that for 400 nm spheres a thin film island over a single template acts individual magnetic unit, whereas for 25 nm template size a collective magnetic structure with domains spread over several particles. There was also a difference in the appearance of magnetism with increasing Fe-deposition: for large template size at the top of the template particle, whereas for the smaller template size at the lateral contact points. The result are summarised in a manuscript appeared in 'Nanoscale' (Merkel et. al, Nanoscale 2015, IF: 7.394).

(iii) Nanostrucutred gold surfaces featuring periodic dome or void structures

By relying on interfacial assembly of particles, we developed a novel and simple method to fabricate metallic nanodome and nanovoid arrays, based on a short annealing of a polymer layer supported particle monolayer template, which has been fabricated by the Langmuir-Blodgett technique (Sepsi et al. Optics Express 2015). These nanostructure metallic surfaces are known to be optically active due to the localised (Mie) and delocalised (Bragg) plasmon modes the support. As a result of the short annealing process the template particles partially submerge into the polymer layer and after an optional removal of the template the structured surface can be coated with a uniform gold film using electron beam evaporation. AFM and SEM measurements show that the prepared structures have a domain-like texture with a typical feature size of 10-20 μm and high local order of the two-dimensional hexagonal lattice within the domains. The measured specular reflectance spectra show a strong absorption band for TM polarizations and a weaker one for TE polarization, which can be attributed to a propagating plasmon mode. Calculated reflectance spectra are in very good agreement with the measured one for all configurations provided incoherent averaging of the theoretical data is performed over all lattice orientations. The good agreement indicates that locally each domain reflects light close to the theoretically predicted reflectance. The results underline the importance of the inherently domain-like structure of self-assembled template structures in general. It also demonstrates that local order at the length scale of a few tens of microns is sufficient to allow the development of spectral features associated with the Bragg plasmon modes. This less strict structural requirement can allow the design and realization of large area optimized surfaces for enhanced light-matter interaction in sensing, energy harvesting and light management applications.

(iv) The interfacial assembled monolayer (Langmuir-Blodgett films) could be also effectively used to pattern mesoporous silica thin films with the combination of Xe+ ion implantation induced structuring. The silica nanoparticle (500 nm) monolayer served as a mask during ion-hammering, that - depending on the energy and fluence of the ions, as well as the porous nature of the underlying sol-gel film - introduced a marked surface topography change (shrinkage) and compacting of the underlying sol-gel film. Confocal fluorescence images and ellipsometric porosimetry measurements confirmed that the contribution of transition zone between the intact masked and damaged regions to the overall porosity of the film is negligible. Furthermore, the majority of the porous volume can be preserved as an interconnected pore system by the application of low ion fluence. By increasing the fluence value, however, separated porous volumes can be created at the expense of the total pore volume. The result were summarised in ‘RSC Advances’ (Albert et. al., RSC Adv., 2015).