Final Report (FK-128327)

The project proposal had two main areas to be addressed (extracted here from the original proposal):

> **I. Patchy nanorparticles**
> Investigation to which extent the patchiness can be controlled for particles with well-developed facets. For this, detailed investigation of the chemical adsorption and ligand exchange process on faceted metal nanoparticles will be carried out. By performing molecular adsorption studies on carefully synthesised, well defined individual nanoparticles and using in-situ optical monitoring of the process the aim is to experimentally investigate how molecules occupy different surface sites as a function of time and molecule concentration at different parts of a nanoparticle.
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> **II. Assembly and particle-particle interactions at the single particle level**
> The main question in this task is related to the effectiveness of the chemical or structural patch (i) to induce the assembly of a given particle, (ii) how effectively the patchiness determines the localization of the bound particle and (iii) how can the fine-tuning of the process carried out relying on factors that alter the strength and range of the determining colloidal interaction.

Hence to address these, gold nanoparticles with different size and shape have been synthesised and their surface modified with various thiol-group containing molecules (here the strong gold-thiol bond is utilized), allowing to introduce permanent surface charges or neutral stabilizers at the particle surface. The process of surface modification and the subsequent, colloidal interaction governed particle aggregation is studied (mainly) spectroscopically both at the ensemble and at the single-particle level. The spectroscopic investigation of these processes becomes possible as a result of the localised plasmon resonance’s sensitivity on the local environment around the particles: any change taking place in the optical near field of the particles (which roughly matches the distance relevant for colloid chemistry) will translate to plasmon resonance related spectral changes.

General comments related to the project

Nanoparticle synthesis and surface modification

Gold nanoparticles with different sizes and morphologies (sphere, rod, bipyramid, prism) were prepared by seed-mediated approach. The state-of-the-art literature synthesis protocols have been continually monitored, implemented and tested in order to obtain the highest quality particles for the experiments. The prepared particles have been purified and characterised by ensemble spectroscopy, dynamic light scattering, and scanning electron microscopy. The aim was here to obtain nanoparticles with well-defined shape and narrow size distribution. The particle dimensions were fine-tuned so that their (dipolar) plasmon resonance wavelength fell in the appropriate wavelength range for the given experiment and had a sufficiently large scattering cross-section (the latter especially important for single particle experiments). Here we had already sufficient routine, so there were no big surprises. Except when there were large contaminations in the campus water system that made nanoparticle synthesis impossible for a few months – probably this also contributed to the complete breakdown of our water purification system. Permission was requested (and granted) form the NRDI Office to buy a new water purification system. Surface modification using thiolated molecules went generally without big issues, but the formation of structural patches (Year3 - “hot-dog” type structural patchy particles) could not be achieved in spite of months of efforts.

There was a general and important change in the project methodology compared to the original Workplan: instead of using Raman or PL active molecules, we could build on a concept very recently emerged in the literature. We could use the inherent chemical interface damping associated plasmon peak broadening induced by thiol adsorption to monitor the ligand exchange process. This huge simplification (no labelling molecule was necessary) was enabled by the improvements of the microspectroscopy setup (see later), which allowed the required spectral accuracy and precision for such measurements (few meV changes have to be measured reliably). This concept can be only applied during single-particles measurements, as otherwise the inhomogeneous plasmon peak broadening masks the small damping change during an ensemble measurement.

Many different molecules have been tested and used for the surface modification, but generally there were those that provided permanent or pH-dependent surface charge (e.g. MTAB, MUA, MPA, MBA) and mPEG-SH, the latter acting as a neutral, steric stabilizer. The combination of a charged molecule and PEG was employed for the patchy particle preparation, so that the charged surface sites were intended to be used as binding sites during assembly, whereas other surface regions of the nanoparticles were effectively shielded by PEG. We also utilized our nanoparticles in other collaborative projects, the topic of which were not strictly related to the presents project, but significantly contributed to its impact.

Substrates and cells for single particle scattering measurements

We struggled a lot to find the appropriate substrates for single-particle measurements.

Mapped substrate have been fabricated at our Microtechnology Department with individually addressed 200x200 micron large boxes. These were perfect for correlative optical/electron microscopy measurements (i.e. the same individual nanoparticles could be easily identified with both techniques). It turned out, however, that the labelling of the mapped substrates (few hundred nanometer thick evaporated Al film) causes some background light scattering in optical dark-field illumination. To get the highest quality optical spectra, we changed to a “pattern-matching” approach, that is, several pictures taken at different magnification have been used to find the area of interest in the optical and electron microscopes. This was much more work, but it was worth it – it provided the highest possible quality of single particle scattering spectra.

Lots of tests have been carried out to find the suitable substrates for the interfacial assembly related works. The main problem was that the even when the nanoparticles have been surface modified with thiol ligand that have a permanent positive charge (e.g. MTAB), the substrates for the self-assembly (glass, ITO, silicone+native oxide) were negatively charged at the conditions (pH and ionic strength), where the bulk-heteroaggregation of the oppositely charged nanoparticles took place. This translated to a very low efficiency (or no) assembly of the negatively charged particles on the substrate supported ones. We experimented with different substrate surface modification (short molecules, polyelectrolytes, neutral cyclic polyolefines) to tackle this issue. The best solutions was to get rid of the substrate surface charge completely by coating the substrates with a few nanometer thin layer of cyclic polyolefine (Zeonex). Unfortunately, this resulted in a hydrophobic surface (DOI: 10.1021/acsomega.9b02990), which complicated particle deposition and led to a rather low surface coverage of the particles, but still enough to carry out particle heteroaggregation at the solid/liquid interface. Due to this delay, no explicit paper on the particle network formation (Scheduled originally for Year4) could be published. This was worsened by the breakdown of the SEM at our institute for 3 months that caused additional delay. Nevertheless there are positive results and there is an MSc work in the pipeline (Gergely Südi) that already contains the first positive results on the directed hetero-assembly of negatively charged (MUA surface modified) spheres and positively charged PEGylated (MTAB/PEG) patchy nanoprisms at the solid/liquid interface. But here more work needs to be done to get a publication out on this specific topic.

Substrates with e-beam lithography generated grooves for the ordered deposition of the nanorods have been also prepared at our Microtechnology Department as planned. The capillary force assisted (ordered and aligned) deposition of the rods, however, proved to be too tedious and has been dropped.

Liquid -cells for the optical microscope

The etched ITO liquid cells have been prepared and tested, by measuring the scattering spectra of individual gold nanorods in inert KNO_3 electrolyte. In the potential range of interest, however, we found that the particles start to dissolve in the interesting potential range, so we dropped the potential control and looked for a new liquid cell type without potential control. We found a semi-commercial solution: we bought from Grace-Biolabs adhesive polycarbonate chambers (150 um high) that can be fit to standard microscope slides and has to liquid ports. Then we modified the optical microscope stage and the dark-field condenser holder so that we can use the cell in our upright microscope. This new cell type was a great improvement as extended duration liquid based measurement could be carried out with easy and programmed liquid (and ligand) exchange protocols in a closed system with the aid of a peristaltic pump.

Simulations and software

Computer simulations have been extensively used and developed during the project, mainly in MATLAB environment. Most work was done on customising an existing package dedicated to plasmonic nanoparticles (MNPBEM). Simulation related improvements:

- We included the nanoparticle size-dependent surface-damping of plasmons in the dielectric function that is fed into the script, allowing to reliably reproduce the broadened spectrum of small particles as well as of their assembled structures.
- For the single particle scattering simulation we managed to implement the limited numerical aperture of the collecting microscope objective, matching a polarisation resolved measurement and the presence of the substrate. This allowed a more rigorous interpretation of the experimental spectra and the capture of fine details during ligand exchange and conclude on the arrangement of the particles upon assembly.
- Simulation of particle-particle colloid interaction at the solid/liquid interface was also implemented in Matlab (with dispersion, electric double layer and steric interaction contributions), which we used to derive design parameters for the assembly experiments (particle sizes, surface charge, substrate charge, PEG chain length, ionic strength).

Other big development has been implemented in the custom written (Labview) measurement control software of the single-particle spectroscopy setup. This became user-friendly (student can now also work with it) with lots of new functions and control possibilities and can now carry out automated measurement of a pre-defined set of individual nanoparticles over extended period of time. Our Microtechnology Department created calibration substrates that could be used to correct for the distortions of the microscope imaging system, for which an image-correcting routine has been implemented. Most importantly, proper calibration of the instrument’s optical transfer function was performed with a dedicated calibration lamp purchased from the project budget, which is a tremendously important feature. It allows to take accurate, calibrated spectra (even in a flow cell) that absolutely match the state-of-the-art internationally.

A fibre-coupled spectrometer control software has been also written from scratch so that time-dependent ensemble optical spectra can be taken during ligand-exchange and self-assembly (heteroaggregation) experiments. Evaluation methods to detect sub-nanometer spectral changes upon ligand exchange or self-assembly have been elaborated and scrips have been implemented to be able to derive the plasmon surface-damping related changes from the single nanoparticles’ scattering spectra. Simultaneously a lot of improvements on the various optical setups’ hardware has been performed.

Scientific works prepared in the framework of to the project (building on Project results)

András Deák:	Self-assembly and optical properties of gold nanoparticles, Doctor of the Hungarian Academy of Sciences (HAS, 2022)
Dániel P. Szekrényes:	Influence of Environmental Inhomogeneities on the Scattering Properties of Gold Nanorods, PhD Thesis (BUTE, 2022)
Dávid Kovács:	Multicomponent Copper(I) Oxide/Gold Nanoparticles and Their Assembly, MSc Thesis (ELTE, 2022)
Dávid Kovács:	Investigation of gold nanorods’ surface modification using microspectroscopy, BSc Thesis (ELTE, 2020)
Dávid Kovács:	Investigsation of molecule adsorption on individual gold nanorods using microspectroscopy, Scientific Student’s Association Conference (ELTE, 2019)
Gergely Südi:	Nanoparticle heteroaggregate formation at the solid/liquid interface, MSc Thesis (BUTE, ongoing, expected date: 2024)
Gergely Südi:	Synthesis and surface modification of gold nanoprisms, BSc Thesis (BUTE, 2021)
Fogarasi Áron:	Investigating ligand-exchange on gold nanoprisms, BSc thesis (BUTE, ongoing, expected date: 2024)
Rita Némedi:	Optimalization of charge-stabilized spherical gold nanoparticle assembly, MSc Thesis, (BUTE 2021)
Rita Némedi:	Investigating the self-assembly of electric double layer stabilised spherical gold nanoparticles, BSc Thesis (BUTE, 2019)
Rita Némedi:	Self-assembly of electric double layer stabilized spherical nanoparticles, Scientific Student’s Association Conference (BUTE, 2019)

Summary of the scientific results

From earlier own and literature studies it was known that local distortions of plasmonic gold nanoparticles’ environment will impact their optical spectrum. For the purpose of the present project we looked for a solid foundation for the impact of local environmental inhomogeneity on the scattering spectra of individual nanoparticles. We created a well-defined, nanopatterned substrate with the combination of nanosphere lithography and ion-implantation to have the substrate dielectric function modulated at a scale smaller than the nanoparticle dimension. Depositing gold nanorods on this patterned substrate and performing correlative SEM/single particle scattering measurements we could correlate the impact of the extent and symmetry of the local inhomogeneity on the scattering spectra (DOI: 10.1021/acs.jpcc.8b07521). It got confirmed, that changes of the plasmon resonance energy and plasmon damping associated peak width changes can be used to indicate the formation of an inhomogeneous dielectric environment around the particles, which in the context of the present project would be the formation of patchy nanoparticles.

Expanding upon these results we investigated how individual particles' plasmon peak shift, but more importantly their peak broadening could be utilized to monitor the ligand exchange process. Recent literature reports indicated that when thiols bind chemically to gold nanoparticles, the polarisation dipole induced by the gold-sulphur bond leads to a broadening of the resonance due the so called 'chemical interface damping' (CID) as the surface scattering of the conduction band electrons at the interface becomes more intense. We tested this CID associated peak-broadening concept with great success and demonstrated for the first time, that this effect can be used to follow fine details of ligand-exchange on individual nanoparticles (DOI: 10.1021/acs.jpcc.0c04629). We could even test conditions that are not easily accessible in the bulk phase during an ensemble measurement (i.e. applying negatively charged thiols to positively charge particle in a broad concentration range without the loss of colloidal stability). We have shown that during the ligand exchange of the original, positively charged CTAB layer with thiols of different charge, positive charged thiols indeed replace the CTAB from the interface, while negatively charged thiols also bind to the surface, but stabilise interfacial CTAB at the same time as well.

We assembled the surface modified nanorods and nanospheres to form heterodimers at the solid/liquid interface and investigated their possible 3D rearrangement (DOI: 10.1039/C9CP01541H). We performed correlative SEM/microspectroscopy investigation to identify heterodimers with different morphology (that is when the nanosphere is located at the side or on-top of the gold nanorod). We implemented polarization resolved scattering spectrum measurement of the individual heterodimers and established the relationship between the scattering spectra features and the relative spatial arrangement of the two particles. With the aid of computer simulation we identified Fano-resonance associated features in the spectra and pinpointed the rod-transversal/sphere-dipole coupled plasmon mode as the main indicator that clearly allows to distinguish between the side and top-arrangements (due to the different orientation of the coupled mode axis). We were also able to demonstrate capillary force induced rearrangement of heterodimers upon drying, which is general importance for solution-based self-assembly procedures.

The surface modification and self-assembly work has been also extended on prism-shaped gold nanoparticles (DOI: 10.1002/ppsc.202200197). This was needed as the ultimate goal of the original Workplan was to investigate the network-formation of the nanoparticles, for which the nanoprisms could be utilized as a 3-directional junction. We used the same concept of patchy nanoparticle preparation as for the nanorods earlier: concentration control of charged thiols combined with the kinetic control of PEG addition was hoped to deliver patchy nanoprisms with the tips/edges functionalised with charged molecules and PEG at the lateral faces of the prisms. From the optical measurements we concluded that this could be achieved for the nanoprisms as well, and also the bulk assembly experiments provided indication for the directed assembly.

We used flow-cell based single-particle spectroscopy to study in detail the ligand exchange process related to patchy gold nanoprism preparation. Compared to ensemble measurements, the CID associated plasmon peak broadening could be also used to characterise the thiol adsorption, and more rigorous interpretation of the spectra became possible using a damped harmonic oscillator model that describes the scattering spectra of individual nanoprisms: we improved the usually applied approach by taking the contribution of the interband transition into account both for the resonance energy and plasmon line width. Consequently, the contribution of thiol adsorption related CID to the resonance shift and the damping change could be separated from other contributing factors. The paper was submitted and is currently with the reviewers in RSC Advances. The submitted paper can be accessed at the following Cloud server links:
Manuscript: https://nc.ek-cer.hu/index.php/s/rmCRzKZ7GsqkwJQ,
ESI: https://nc.ek-cer.hu/index.php/s/WE8nfZaxe9eeXDD.
Abstract:

> „The attachment of thiolated molecules onto gold surfaces is one of the most extensively used and robust ligand exchange approaches to exploit the nanooptical features of nanoscale and nanostructured plasmonic materials. In this work, the impact of thiol adsorption on the optical properties of wet-chemically synthesized gold nanoprisms is studied both at the ensemble and single particle level to investigate the build-up of more complex ligand layers. Two prototypical ligands with different lengths have been investigated ((16-mercaptohexadecyl)trimethylammonium bromide – MTAB and thiolated polyethylene glycol – mPEG-SH). From ensemble experiments it is found that composite ligand layers are obtained by the sequential addition of the two thiols, and an island-like surface accumulation of the molecules can be anticipated. The single particle experiment derived chemical interface damping and resonance energy changes further support this and show additionally that when the two thiols are used simultaneously, a higher density, intermixed layer is formed. Hence, when working with more than a single type of ligand during surface modification, sequential adsorption is preferred for the combination of accessible essential surface functionalities, whereas for high overall loading the simultaneous use of the different ligand types is favourable.”

As the next step we moved towards the directed assembly at the solid/liquid interface using properly surface modified nanoprisms and spheres, this work is still under way, the first positive results are summarised in an MSc thesis under preparation, but more work will be done to get enough material for a paper.

Throughout the work, PEG-SH was used as a steric stabilizer that can effectively block attachment to particle surface sites that are covered by this molecule. As written above, the concept was generally to utilize PEG on non-spherical particles (rods, prisms) at given surface-sites to block particle attachments in these regions. But we also prepared spherical PEGylated particles to address various scientific questions that arose during the work.

We investigated e.g. the controlled assembly on PEG-only covered nanoparticles in the presence of salt at elevated temperature. In was known from earlier studies that this leads to homoaggregation of the spheres due to a modification of the colloidal interaction between the particles upon PEG-chain collapse. But we intended to gain a better insight into the structure of the evolving nanoparticle clusters and hence carried out systematic SAXS and optical spectroscopy studies supported by simulations. We could find solid correlation between the in-situ measured SAXS and the optical data, which interestingly indicated the formation of kinetically trapped, few-particle clusters upon initiating the particle clustering instead of the growth of large, monolithic aggregates (DOI: 10.1039/D2SM01257J).

PEG-coating of the nanospheres also allowed the preparation of a well-defined nanoparticle monolayer at solid substrate by the Langmuir-Blodgett technique. This we could utilise as a supporting substrate to generate corrugated graphene layers. The corrugation length dictated by the gold nanoparticles created strain the graphene, whereas to PEG-coating still acted as a spacer preventing direct contact between the gold nanoparticles and the graphene sheet (DOI: 10.1016/j.cartre.2021.100080).

In terms of the research goals of the current project, our recent work related to gold/Cu_2O heteroparticles is rather off-topic (it deals with the particle-structure determined fate of photoexcited charge carries and their photocatalytic properties), but it builds on the gold nanoparticles and the single-particle optical setup as well as on the optical simulation developed in the framework of the present project. We could identify the (coupled) plasmonic and Mie-modes of the heteroparticles and provide the interpretation for their optical spectra that displays many features with different origins (DOI: 10.1039/D3TC01213A).

Another work where our expertise in optics and physical-chemistry could be utilized was also related to gold/graphene heterostructures. With colleagues from our institute the we studied the plasmon related optical changes upon exposing the nanoparticle heterostructures to different organic solvent vapour (ethanol, 2-propanol, toluene). Changes in the dielectric environment around the particles and capillary condensation could (in part) explain the observed spectral changes and the sensitivity difference of the implemented optical detection scheme (DOI: 10.1039/C9NA00110G). In collaboration with the same group we also utilised our nanoparticles to modify the reflection properties of natural photonic crystal architectures (DOI: 10.3390/photonics9080553). In another collaborative project where we contributed with our project-related expertise on nanoparticle light-scattering and nanoparticle interaction was related to the periodic precipitation of particles and formation of Liesegang patterns (DOI: 10.1021/acs.jpcb.2c05810).

In a very recently accepted paper (‘Oppositely Charged Nanoparticles Precipitate Not Only at the Point of Overall Electroneutrality’, accepted on 26.09.2023 in The Journal of Physical Chemistry Letters) we also investigated the electric double layer interaction induced heteroaggregation of oppositely charged nanoparticles in detail and provided an interpretation for the particle size-dependence of the process.

As a plus, we could also utilise our calibrated microspectroscopy setup developed in the project to perform high precision, high spatial resolution temperature mapping of micro-hotplates prepared at our Microtechnology Department.

In summary, the research goals have been largely achieved during the work, with some work still underway form Year4 of the Workplan (interfacial assembly at the solid/liquid interface). Difficulties that arose could be tackled or circumvented and several interesting side-projects could be also realised. The Group profited a lot during these year from the project. The involvement of students was successful, and several theses could be delivered. Besides the scientific output, many crucial methodological and infrastructural improvements could be implemented.