DIRECTED SELF-ASSEMBLY OF GOLD NANOPARTICLES:
NANOPARTICLE CLUSTERS AND 2D ORDERED NANORINGS

Theses

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1 INTRODUCTION

The special optical properties of gold nanoparticles (NPs) due to their ability to support localized surface plasmon resonance (LSPR) are well-known. The phenomenon of LSPR is originating in the resonant oscillation of conduction electrons, as the metal nanoparticle interacts with the incident light. Experimentally, this results in an intensive extinction peak in the visible spectrum, which can be fine-tuned by the shape and size of the particles and the dielectric properties of the embedding medium in turn. Upon two particles approaching each other, their near-fields can interact and the frequency of the resonance (red)shifts. This phenomenon is called plasmon coupling. Due to the extent of the coupling is highly sensitive to the interparticle separation distance, an eventually occurring association (formation of higher order structures) can be easily followed by spectroscopic techniques.

The surface of gold nanoparticles can be effectively modified by numerous types of molecules in order to render the surface improved functionalities. Gold shows high affinity to molecules containing thiol or amino end groups, allowing to bind responsive polymers covalently or semi-covalently. Responsiveness of surface attached molecules enables to modulate the colloidal interactions between the nanoparticles. Modulation requires keeping the attractive and repulsive interparticle potentials under control. For the systems considered in the present work, attraction is mainly associated with van der Waals (vdW) forces, while repulsion can originate in electric double layer (EDL) interaction and/or steric repulsion due to the surface attached polymers.

According to the classical DLVO (Derjaguin-Landau-Verwey-Overbeek) theory, the stability of the nanoparticles in an aqueous solution can be described based on the attractive van der Waals and the repulsive electric double layer interaction. However, in order to prepare a compact nanoparticle cluster, a soft-sphere type interaction potential is required [1], which cannot be achieved by solely considering the above two types of interaction. Relying on steric repulsion at small separations, however, can effectively counterbalance the large vdW attraction, leading to the desired interaction profile. Steric interaction is usually related to the presence of (macro)molecules on the nanoparticle surface, which allows to properly design the total interaction and create the soft sphere type interaction curve. A negative interaction potential will ensure that the particles approach each other, but the structures developed during the assembly process are highly dependent on the magnitude of this driving force. If the driving force is too large, the classical, fractal like aggregates are formed due to diffusion limited aggregation. That is, the minimum requirement for any directed assembly procedure is an effective control over the magnitude of this attraction. This translates to the crucial importance of appropriately pre-designed nanoparticles and on-demand modulation of the NP-NP interaction potentials.

Whereas the vdW attraction is always present and fairly independent on the relevant environmental (solvent) parameters. The EDL interaction on the other hand is easily modified by changing the charged nature of the particle surface or the shielding of the electric potential e.g. by the ionic strength of the medium. For the modulation of the steric interaction, the use of thermoresponsive polymers offers a convenient solution, where – depending on the temperature of the system – the molecules accommodate a different conformation. This allows for an effective modulation of the total interparticle potential,

that allows to trigger or control nanoparticle assembly. Poly(ethylene glycol) derivatives are commonly used to stabilize gold nanoparticles, which has a lower critical solution temperature (LCST). The LCST can be reduced applying increased ionic strength \[ 2 \].

The structure and ordering of the aggregates and the kinetics of the formation of assemblies depend on the interparticle potentials sensitively.

During self-assembly of nanoparticles, higher-order structures evolve in the solution or at interfaces, which allows to exploit the special optical properties based on the closeness of the building blocks. Due to plasmon coupling, extremely high local electromagnetic field enhancements might arise, with potential applications in the field of theranostics [3] or surface enhanced Raman scattering (SERS) [4,5]. Especially for SERS, formation of high-quality, ordered structures (e.g. nanorings from gold nanoparticles) on an appropriate substrate is of crucial importance. Beside the numerous lithography-based technique [6,7] (which are reliable and well-controlled, but time consumptive and expensive), these kind of structures can be produced on colloid chemical bases [8]. However, it is challenging to prepare them reproducibly and reliably, because the wettability and surface energies of the components, the temperature, the purity of the system and the drying circumstances have to be controlled during a capillary lithographic process.

Variety of structures can be formed upon clustering, which have complex optical response [9]. Consequently, simulation techniques have been become more and more important to understand these complex optical properties of nanostructures through simulation of simpler model systems.

## 2 AIMS

My aim was to design a nanoparticle system, which fulfills the requirements for a soft-sphere type interaction and allows proper control over the net colloidal interaction so that it can be utilized to study the directed assembly of nanoparticles in detail and to achieve nanoparticle assemblies with different morphologies (oligomers, large ordered 3D clusters, 2D single particle rings). Spherical gold nanoparticles surface modified with polymers containing thiol and amino functional group have been used for the directed self-assembly experiments. The surface-attached thiolated- and aminated methoxy-poly(ethylene glycol) (mPEG-SH and mPEG-NH\(_2\)) polymers were used to provide steric stabilization. Due to the developed thermoresponsive approach involving mPEG, its conformation can be tuned by combined stimulus.

My detailed aims can be summarized in the following points:

- Developing nanoparticles that are capable to interact with each other via a tunable, so-called ‘soft-sphere type’ interaction\(^1\) was targeted, where the on-demand

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modification of the colloid interaction potential should be realized in a controlled way. This would result a model system that allows a wide range of experimental investigations connected to the pre-engineered clustering of nanoparticles upon applying external stimulus. To achieve this goal, the otherwise well-known concept of solubility change of macromolecules in the presence of dissolved ions and elevated temperatures was planned to be exploited (Figure 1a).

- Since the assembly of nanoparticles in general inherently involves the (partial) loss of their stability, control over the interparticle potentials is essential. It was investigated, whether the above developed nanoparticle system could be used for the verification of earlier theoretical predictions\(^2\), \(i.e.\) for the preparation of ordered, three dimensional nanoparticle clusters from a bulk solution. According to theory, this requires a soft-sphere type interaction between the nanoparticles, that is attraction at larger separations but a pronounced repulsion at small particle-particle distances. The developed nanoparticle system was designed with a view on this theoretically predicted constrain, and systematic investigations (varying the triggering factors) were designed. Prior to the experimental work excessive colloidal interaction calculations were planned to theoretically predict the suitable system for the experiments. By correlating experimental and theoretical data, a better understanding of the connection between the resulting cluster structures and the clustering process itself was envisaged (Figure 1b).

Figure 1. Concept of directed self-assembly of mPEG-covered gold nanoparticles.

- Since the mPEG grafted AuNPs described above proved to be extremely stable against spontaneous aggregation or adsorption at interfaces, their potential as tracer objects for studying capillary lithography was investigated (Figure 2). During the capillary lithography process, the drying and dewetting associated receding of the suspending liquid is responsible for the obtained nanoparticle deposits. With the aid of the gold nanoparticles, different dewetting stages and the overall mechanism of capillary lithography was planned to be elucidated. Information about the dependency of the nanoparticle spatial distribution on the different parameters (substrate type, template size, particle concentration, temperature, defects in the template monolayer) was planned to be obtained. Additionally, the possibility to prepare two dimensional, ring shaped nanoparticle clusters by this approach was investigated as well.
Self-assembled gold nanoparticle systems usually have a complex optical response due to plasmon coupling. By performing optical simulations (based on boundary element method) of different nanostructures that are relevant in the current context of the experiments (chain-like oligomers, 2D heptamers and 3D clusters), a better understanding of the experimentally obtained optical spectra was targeted. Another aim was to clarify, to which extent the experimentally measured extinction spectra are applicable in obtaining structural information about the particle clusters during a real assembly process (Figure 3).

For the experimental part of the work, gold nanoparticles were synthesized in six different sizes as model systems. The smaller particles were prepared by the traditional Turkevich method [10], the larger ones were synthesized from the 18 nm and 40 nm particles according to the seeded-growth method published by Ziegler et al [11]. Nanoparticles surface was modified using two types of poly(ethylene) glycol with different end groups (thiol and amino). After the process, particles were purified applying centrifuging-redispersion cycles; size, ζ-potential, visible light spectrum and concentration were measured as well.

For externally triggered clustering, 18 and 40 nm gold nanoparticles covered by mPEG-SH were used. Prior the experimental work, possibility of clustering was predicted performing calculation of net interparticle potentials including three main interactions: attractive van der Waals, electric double layer repulsion and steric repulsion. Self-assembly was investigated experimentally adding K$_2$SO$_4$ solution to the nanoparticles in different concentrations (0 M - 0.3 M) and increased temperature as triggering factors.

Aggregation was followed by DLS and visible light spectroscopy. The structure of the resulting clusters was investigated by SEM and TEM.

The kinetics and the structure of the clusters during the perturbation induced assembly were followed by time-dependent spectroscopy and time-dependent DLS measurement for 20 nm gold nanoparticles modified by mPEG-NH₂. Self-assembly of the building blocks were investigated at different ion concentrations and increased temperatures. Structure of the evolved assemblies was characterized by SEM. In order to analyze the cluster sizes at different conditions semi-quantitatively, image analysis was performed on low-magnification SEM images as well. Stability of the aggregates was investigated against external source of energy (ultrasonication).

PEGylated gold nanoparticles in diameter of 18, 45 and 65 nm were used as tracer objects to identify dewetting stages during capillary lithography experiments. Additionally, single chain gold nanoparticle rings on silicon substrates were produced. Colloidal lithographic experiments were performed by drying nanoparticle solution in appropriate concentration on a template monolayer of polystyrene (sub)microparticles prepared by Langmuir-Blodgett technique. Diameter of PS beads was varied from 608 nm to 2.48 μm. Capillary forces organize the NPs underneath the PS particles during the drying resulting nanoparticle chains which can be developed by removing the LB-film. Relationship between internal diameter of nanorings and diameter of template particles was shown based on SEM image analyses and geometrical calculations. Stages of drying, nanoparticle deposits and the effect of defects in the template monolayer were analyzed by SEM.

Optical simulations of self-assembly relevant gold aggregates were performed by boundary element method (BEM) [12]. Chains composed of different number of NPs, 2D heptamers and 3D clusters were investigated in silico. The nanoparticles surfaces were discretized using 400 vertices, the embedding medium was set to water (dielectric constant: 1.776), the dielectric function of gold nanoparticles was used from the work of Johnson and Christy [13]. Simulations were validated by performing calculations using Mie-theory. The diameter of the particles was 18 and 40 nm, while the interparticle separation distance was varied from 0.2 nm to 3.8 nm and 0.8 to 10.0 nm, respectively. To highlight the coupled nature of these structures, near field maps were calculated at different wavelengths to visualize the enhancements. To obtain the complex optical response of a fractal-like aggregated system (diffusion-limited aggregation), citrate-stabilized 18 nm gold nanoparticles were aggregated using K₂SO₄ solution in high concentration (0.3 M).

4 RESULTS

4.1 Preparation of compact NPCs from PEG-coated gold NPs [S1]

4.1.1 Modeling of interparticle colloidal interactions

For calculation of net interparticle potentials attractive van der Waals force, electric double layer repulsion and steric repulsion were taken into account. Attraction is essentially programmed into the system through Hamaker constant, electric double layer thickness can be controlled by varying ionic strength of the medium, however, steric repulsion depends on the conformation (namely the chain length) of surface attached mPEG molecules. Polymer brush thicknesses were assumed based on DLS size measurements (Table 1).

Table 1. Polymer brush thickness values as measured by DLS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (nm)</th>
<th>Difference (nm)</th>
<th>Polymer brush thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP1</td>
<td>17.7</td>
<td>3.7</td>
<td>1.85 ± 0.1</td>
</tr>
<tr>
<td>GNP1@mPEG-SH(750)</td>
<td>21.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GNP2</td>
<td>39.9</td>
<td>13.8</td>
<td>6.9 ± 0.3</td>
</tr>
<tr>
<td>GNP2@mPEG-SH(2000)</td>
<td>53.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Modulation of steric interaction via external stimuli (increased ionic strength and temperature) can open up possibility to modulate the total NP-NP potential leading to destabilization of the particles. In order to map the possible depths of interaction, total NP-NP interaction energies were calculated for different mPEG brush thicknesses using the initial thicknesses obtained from Table 1 (Figure 4).

Figure 4. Calculated total interaction energies as a function of mPEG brush thickness for (a) AuNP(18nm)@mPEG-SH(750) and (b) AuNP(40nm)@mPEG-SH(2000) at 60°C.

The insets show the energy minima for different brush thicknesses.

These calculations indicate that chain collapse and the collateral net interaction modulation act like a significant driving force of clustering. In addition, the increased electrolyte concentration and temperature can be used for triggering the assembly externally.

4.1.2 Externally-triggered clustering of gold NPs

Temperature-induced clustering of gold nanoparticles was investigated by DLS, where size evolution of the system was followed at different ion concentrations. DLS size distributions as a function of temperature were transferred to a unique contour plots.
(Figure 5) for each ionic strength, where colors represent the DLS intensity. A vertical cross section of these plots gives the conventional size distribution at a given temperature.

![Figure 5. Contour plots demonstrating DLS size distribution of AuNP(18nm)@mPEG-SH(750) as a function of temperature for different K$_2$SO$_4$ concentrations: (a) 0.15 M, (b) 0.20 M, (c) 0.25 M and (d) 0.30 M. Color bars represent the intensities measured by DLS. Aggregation becomes intensive at 0.30 M, where the population with initial particle size decreases continuously above 30 °C beside the appearance of a second population with larger size. At moderate salt concentrations (0.20 and 0.25 M) the aggregation is more discrete: a sudden increase of size can be observed above a threshold temperature.

![Figure 6. Evolution of extinction spectra for (a) AuNP(18nm)@mPEG-SH(750) at 55 °C and (b) AuNP(40nm)@mPEG-SH(2000) at 60 °C in time. Electrolyte concentration was set to 0.30 M for both samples. Evolution of extinction spectra of smaller and larger particles were followed in time as shown in Figure 6. In these experiments the temperature was set based on the threshold temperatures determined from above presented DLS measurements. Aggregation is indicated by the decrease of the single particle LSPR and emerging a new plasmon peak.](image-url)
at higher wavelengths (750 and 650 nm, respectively) related to the plasmon coupling between particles in close proximity. SEM images of resulting clusters and aggregates are presented in Figure 7, where the differences between the structure of aggregated mPEG-covered and citrate-capped NPs can be seen nicely. While the polymer-coated particles form compact, denser clusters, the aggregated citrate-stabilized NPs have a fractal-like structure. It can be explained by the different thermodynamic driving force that influences the structure of resulting clusters significantly. Large attractive potential causes fractal-like aggregates, because the building blocks become kinetically trapped and their reconfiguration in the cluster is not allowed.

![SEM images of resulting clusters and aggregates](image)

**Figure 7.** Scanning electron microscope images of compact nanoparticle clusters prepared from (a) AuNP(18nm)@mPEG-SH(750) and (b) AuNP(40nm)@mPEG-SH(2000). Fractal-like aggregates of citrate-coated 18 nm gold NPs used as control sample (c). The insets of panel a and c show close-ups of the clusters and have a width of 120 nm.

### 4.2 Aggregation kinetics and cluster structure of aminoPEGylated gold NPs [S2]

Aggregation kinetics of mPEG-NH₂ coated gold nanoparticles was investigated by time-dependent spectroscopy (Figure 8) and time-dependent DLS at different ion concentrations and temperatures. Figure 8 represents the differences of time-dependent spectral properties of the model systems after the perturbation. At 0.2 M and 50 °C the spectrum does not change significantly in time and only a minor shoulder starts to evolve around 570 nm, which can be attributed to a small fraction of clusters contain only few nanoparticles. However, at 0.3 M, the initial LSPR redshifts in the first period of clustering (2 minutes), which refers to a fast aggregation kinetics.

![Evolution of extinction spectra](image)

**Figure 8.** Evolution of extinction spectra for Au(20nm)@mPEG-NH₂(2000) at different salt concentrations and temperatures.

Average hydrodynamic size and count rate plotted together (Figure 9) as a function of time shed also light on the differences between kinetics. For 0.2 M and 50 °C only a slight increase in size can be observed that followed by an increase in the count rate (scattering) which represents the size is strongly weighted to the larger scatterers in the solution. In case of 0.3 M and 60°C, the system behaves differently: the size increases...
significantly faster and only the stage after the transition point of count rate function can be resolved due to the fast kinetics.

Figure 9. Average hydrodynamic size and count rate measured by DLS as a function of time at different salt concentrations and temperatures.

Structures of the evolved clusters were investigated with SEM, from which the structures formed at 0.2 M and 50 °C and 0.3 M and 60 °C are demonstrated in Figure 10. Small compact assemblies of few NPs were formed at 0.2 M and 50 °C, which observation is in a good agreement with the spectral features of this sample showing only broadening and slight redshift. The largest NPCs can be obtained at the highest ion concentration and temperatures, and here can be found the least number of individual NP.

Figure 10. Structure of the clusters at different electrolyte concentrations and temperatures: (a) 0.2 M, 50 °C; (b) 0.3 M, 60 °C. Insets show the compactness of the structures.

Additionally, at 0.2 M, 50 °C the population of the initial particles (individual building blocks) can be partially recovered by 5 minutes of sonication, larger clusters show only fragmentation without the appearance of monomer particles (Figure 11). This observation indicates a difference in NP-NP interaction energy related to the two systems.
4.3 Identification of dewetting stages and preparation of single chain nanoparticle rings by colloidal lithography [S3]

Stages of drying after the wetting of template monolayer with aqueous gold nanoparticle solution were identified based on SEM images. Dewetting stages and characteristic particle deposits are summarized in Figure 12. During initial stage of drying, menisci are formed between neighboring template particles generating liquid bridges parallel to the substrate. This results remaining particles trapped at the lateral contact point of the particles (green square). Liquid level exceeds the equatorial plane of the particles which induces a faster evaporation in the triangular openings due to the ‘chimney’ effect.

This manifests in gold NP deposits at the triple points on the substrate (red square). During further evaporation, liquid film starts to evolve between neighboring PS particles and the silicon substrate, but these particles cannot be investigated from top-view. After the suspended film breaks up, liquid bridges evolve between neighboring particles whose thinnest point can be found at the midpoint between two PS particle. This occurs random deposition of nanoparticles along the triple line, but trapped ones at the midpoints (purple square).

In the final stage of the drying, the volume of these circular films decreases and the nanoparticles will be pressed into the wedge between PS and the substrate. Finally, the nanoparticles accumulate in a circular shape underneath the template particle forming single chain nanorings. Nanorings formed from 45 nm and 65 nm Au NP and different PS template particle sizes are demonstrated in Figure 13a-d. Diameter of produced nanorings shows dependency on the template particle diameter: using smaller PS beads smaller nanorings can be created. The internal diameter of gold nanorings can be estimated theoretically as well. Calculations and real internal diameters have excellent agreement demonstrated in Figure 13e.
Figure 12. Stages of the dewetting process below the equatorial plane of the template particles. Left panel shows the top view of the unit cell, where dashed lines indicate the plane of cross sections showed in the middle panel. (a) Nanoparticle trapped at the triple point, where the liquid film is the thinnest; (b) assumed particle trapping at the thinnest point of the liquid bridge between two neighboring template particles; (c) nanoparticles trapped at the midpoint of the liquid bridge. SEM images of colored regions are represented in the right panel.

Figure 13. Single chain gold nanoparticle rings of (a,b) 45 nm and (c,d) 65 nm nanoparticles under (a) 608 nm, (b) 909 nm, (c) 1.27 μm and (d) 2.48 μm PS particles. (e) Calculated (solid line) and measured (scatter plots) internal ring radii in a function of template radius. Inset shows the calculation parameters according to hard sphere contact model.

Effect of local defects and defect sides in template monolayer on the resulting structure was also investigated. Vacancies in the monolayer induce NP accumulation in the middle
of the vacancy according to the “chimney” effect (Error! Reference source not found.a). Line defects indicate particle deposition between four PS particles (Error! Reference source not found.b). Domain boundaries cause broad disordered regions, where the surface coverage of the microparticles is smaller and the hexagonal order is missing. Here random depositions, thick rings and connected wires can be observed (Error! Reference source not found.c).

Figure 14. Effect of vacancies (a), defect sites (b) and domain boundaries (c) on the structure after the drying process.

4.4 Optical simulation of self-assembly relevant gold assemblies

In self-assembly processes, numerous different optically dominant structures can be evolved such as 1D-chains, 2D-heptamers and 3D clusters. In order to determine the unique optical response of different aggregate structures, optical properties of model-structures (with different gaps between the particles) were simulated using boundary element method (BEM) in the visible wavelength range. To identify the plasmon coupled mode in the simulated extinction spectra, near-field of the structures were investigated at appropriate wavelengths. Simulated model systems can be seen in Figure 15.

Figure 15. Schematics of simulated nanostructures containing N nanoparticles: (a) chains containing different number of particles, (b) 2D-heptamers and (c) 3D-clusters (A-B-A type close packed structure). The separation distance (D) between the particles was varied.

Figure 16a summarizes the optical response of gold nanoparticle chains composed of 7 particles with diameter of 40 nm at different separation distances. For large separation (3.80 nm) the particles are relatively far from each other, thus the plasmon coupling is weak and does not influence the individual particle spectra significantly. When the gap decreases, new peak at higher wavelengths starts to evolve for all chain lengths due to plasmon coupling effect. Near-field map proves, that the peak at higher wavelength
corresponds to the strongly coupled mode: significant enhancement (well above 50) can be observed.

Figure 16. Simulated extinction spectra of (a) linear chain composed of 7 particles, (b) 2D heptamer and (c) 3D cluster at different interparticle separations. Near field maps at 1.60 nm separation and different wavelengths are demonstrated in the bottom row: 537 nm and 645 nm for chain, 526 nm and 580 nm for heptamer, 560 nm and 670 nm at different planes (top and side view) for 3D cluster.

Extinction spectra of heptamers were simulated for 40 nm particles at different separation distances (Figure 16b). At large separation distances, the spectra correspond to the extinction spectrum of an individual particle. However, decreasing gap causes slight redshift, broadening and evolution of coupled mode even at short distances. Near-fields confirm that only slight coupling can be observed at 526 nm, while the enhancement becomes much higher at 580 nm, thus this can be identified as the coupled mode in the extinction spectrum.

Simulation results of 3D clusters built from 40 nm particles with varied separation distances are demonstrated in Figure 16c. Spectra for larger separations are similar to the spectra of single nanoparticles, however they become more complex at decreased gaps, where new coupled features can be observed. As can be seen in the near field map, a significantly larger enhancement evolves at 670 nm.
THESES

The novelty of the work can be summarized in the following theses:

1. I developed a new approach to realize the controlled aggregation of gold nanoparticles with diameters larger than 18 nm in aqueous medium. It is based on the reduced interparticle steric repulsion associated with 750 Da or higher molecular weight poly(ethylene glycol) molecules, when the medium contains K₂SO₄ and the temperature is increased above 50 °C. The phenomenon behind the changing of the steric repulsion is the conformation change of the polymer chains (chain collapse). I was the first to apply this concept for the preparation of compact gold nanoparticle clusters. [S1]

2. I confirmed using colloid interaction energy calculations, that the fact of the aggregation and the ordering of the evolved nanoparticle cluster structure can be explained by the decreasing steric repulsion in the given systems. The variety of the evolved structures originates in the soft-sphere type interaction and the moderate energy minimum with few kT depth. Consequently, it can be utilized – in contrast to the structures evolving during diffusion-limited aggregation – to prepare compact gold nanoparticle clusters. [S1]

3. I confirmed, that the aggregation kinetics of 20 nm gold nanoparticles covered with amino poly(ethylene glycol) can be controlled by changing the temperature and ion concentration of aqueous medium. Both the temperature and the ion concentration speed up the aggregation, however, the effect of ion concentration on the aggregation kinetics is more significant. The different aggregation kinetics obtained at increased ion concentration and elevated temperature originates in the change of the interaction between mPEG chains. [S2]

4. I showed, that the structure of nanoparticle aggregates evolved at increased ion concentration and elevated temperature from 20 nm gold nanoparticles covered with amino poly(ethylene glycol) shifts from the small oligomers towards the larger, 3D clusters. I followed the formation of aggregates and it was confirmed, that nanoparticles from smaller oligomers can be partially recovered applying external source of energy (ultrasonication), however, the larger clusters only fragment. [S2]

5. I pointed out the correlation between dewetting process and the resulting structure during capillary lithography using mPEG-coated gold nanoparticles between 18 and 65 nm in diameter as tracer objects. From local ordering of the particles (nanoparticle deposits), I identified the stages of the drying and the effect of template monolayer defects (point and line defects, domain boundaries) on the resulting structure that originate in the nanoparticle trapping induced by the receding liquid bridges between the substrate and the template particles. [S3]

6. I prepared two-dimensional arrays of single chain gold nanoparticle rings using capillary lithography. The array was prepared using gold nanoparticles and polystyrene template particles in different sizes. I confirmed, that the internal radii of gold nanorings can be tuned by the size of the template and the nanoparticles. [S3]

7. I performed optical simulations of relevant structures (1D chains, 2D heptamers and 3D clusters) evolving during the aggregation of PEG-covered gold nanoparticles in different sizes. The extinction spectra of the above mentioned structures were simulated by boundary element method. The results draw attention to the fact, that a presence of a structure cannot be evidenced solely from the optical response of the
nanoparticle system, because similar optical responses can be obtained for different structures as a function of interparticle distance. [S4]

6 PUBLICATIONS

6.1 Publications related to the dissertation


[S4] Zámbó D.; Deák A. Optical Simulations of Self-Assembly Relevant Gold Aggregates: A Comparative Study. *Periodica Polytechnica Chemical Engineering* 2016, accepted manuscript (IF=0.296)

6.2 Other publications


6.3 Presentations


6.4 Posters


