Patchy gold nanoparticles: programmed preparation, characterization and self-assembly

Theses

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1 Introduction and Aims

Deep understanding of self-assembly processes in nanoparticulate-systems is gaining more importance in a variety of research fields related to nanotechnology. Achieving precise control over the structure of nanoparticle assemblies is a challenge to face. The majority of nanoscale assembly procedures rely on the intrinsic surface properties and morphology of the building blocks. Complex materials composed of oriented structures of nanoparticles have additional properties compared to single particles and a number of applications could benefit from it, for instance catalysis, optoelectronics and biomedical applications.\(^1,2\)

The preparation of gold nanoparticles with inhomogeneous surface chemistry or structure and the investigation of self-assembly processes are the main aspects of the dissertation. One of the simplest anisotropic nanoscale objects are rod shaped nanoparticles. The number of acting particles and their relative orientation have highly specific effect on the optical properties of nanostructures performed by directed assembly of gold nanorods. This can be exploited to determine correlation between the discrete assembled structure and the optical response. Cetyltrimethylammonium bromide (CTAB) stabilised gold nanorods offer the possibility for the preparation of patchy particles with region-selective surface modification due to the less compact ligand shell at the tip region. Treating the tip region of the NRs with charged thiol molecules can enable the preparation of tip-assembled superstructures.\(^3,4\)

One of the aims of the work was the development of a two-step surface modification procedure in order to prepare patchy gold nanorods with positively charged tip regions, while the side of the rods is covered by surface grafted PEG. Secondly, my aim was to achieve directed self-assembly between the nanorods with complex surface chemistry and gold nanospheres with homogeneous surface properties (Figure 1a.). In order to explore the limitations of self-assembly my aim was to investigate the effect of increased sphere size and salt concentration on the evolved structure.\(^1\)

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(2) Guo, X.; Zhang, Q.; Sun, Y.; Zhao, Q.; Yang, J. Lateral Etching of Core–Shell Au@Metal Nanorods to Metal-Tipped Au Nanorods with Improved Catalytic Activity. ACS Nano 2012, 6 (2), 1165–1175 DOI: 10.1021/nn203793k.
Figure 1. a) Preparation steps of patchy gold nanorods and their self-assembly with citrate stabilized spheres. b) In situ investigation of rod/sphere heterodimers with single-particle scatterometry in liquid cell.

The intense scattering of the particles allows direct observation and spectral characterization at the single particle level, especially when the rod particle dimension exceeds ca. 40 nm. Accordingly, rods with larger diameter are optimal scatterers for investigating the characteristics of self-assembly processes, especially gold nanosphere adsorption (Figure 1b). In situ measurements performed in the liquid cell open the possibility for gaining direct information about how the self-assembled structure evolves in the aqueous phase. Furthermore, both the directing feature of colloidal interactions and immersion type capillary forces can be investigated separately.

Figure 2. Schematic illustration of the multistep Janus particle synthesis procedure.

Janus particles represent a more complex group in the category of anisotropic building blocks. Generally, Janus particles have approximately 1:1 distinct coverage in shape, composition, chemistry, polarity and functionality. The additional properties arising from complexity can be exploited in self-assembly to create well-defined patterns. In these self-assembled structures the number and spatial arrangement of the building blocks can be controlled via particle parameters. For the latter aspect, my aim was to develop hybrid silica-

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gold nanoparticles with mushroom-like Janus morphology, with excellent control over the resulting particle geometry, especially the coverage and cap thickness (Figure 2.).

2 Methods

Gold nanoparticles used in self-assembly experiments were prepared by wet-chemical synthesis procedures. Citrate-stabilized gold nanospheres were synthesized in three different sizes based on seed-mediated protocol developed by Yoon et al.\textsuperscript{5,7} For bulk experiments and self-assembly performed in liquid cell, CTAB stabilized gold nanorods were prepared in four different aspect-ratios according to previously published seed-mediated protocol.\textsuperscript{8} The different dimensions were achieved by adjusting the synthesis parameters and using additives (hydrochloric acid and sodium-oleate\textsuperscript{9,10}). The as-prepared gold nanoparticles were monitored using a fibre coupled UV–Vis spectrometer, the extinction spectra of the different sphere and rod solutions are summarized in Figure 3.

\textbf{Figure 3. Extinction spectra of gold nanospheres (left) and nanorods (right) used in self-assembly experiments.}

During the surface modification, optimal cysteamine and mPEG-SH concentrations were determined by the gold nanorods’ properties. The ligand exchange was monitored by spectrophotometry and electrokinetic measurements, the latter was performed by dynamic light scattering. After the surface modification process the prepared patchy particles were used in self-assembly experiments after purification by repeated centrifugation/redispersion steps. For the spectral measurements in bulk, the solution of patchy nanorods and nanospheres were mixed to result a nanosphere:nanorod molar ratio of 10:1.

The sample preparation for the SEM analysis was implemented by spin-coating. By drop-casting the nanosphere solution onto the substrate self-assembly has been taken place. For in situ investigations of the self-assembly process, liquid chamber with patchy nanorods immobilized on an ITO substrate was prepared. The particle-covered substrate was used as the bottom plate, a spacer (Parafilm) and a standard 0.1 microscope cover slide were used to complete the liquid chamber. After a short heat-treatment the chamber was fixed by molten spacer providing approximately $100 \mu m$ gap between the ITO substrate and the cover slide. The single-particle spectroscopic measurements in transmittance mode were performed by an upright optical microscope (Olympus BX51) equipped with an oil-immersion dark-field condenser. In the optical microscope, the light source provides high intensity in the VIS-NIR range and the trinocular observation tube transmits the light also in the same region, therefore
the spectral shifts around the nanorod’s longitudinal LSPR peak (approximately 700 nm) can be safely investigated. The stage was set to an area displaying well separated individual scatterer. The chamber was filled with ultrapure water first and the scattering spectrum of selected individual nanorods measured using an imaging spectrograph (Princeton Instruments Isoplane SCT320) equipped with a high sensitivity CCD detector (Princeton Instruments PIXIS:400BRX). The flow cell was flushed with the solution containing the spherical particles. After 5 minutes, the cell was extensively flushed with water again until no free spheres undergoing Brownian motion could be observed, to remove unbound nanospheres hence avoiding non-specific interactions between the particles during drying of the sample. Dark-field scattering spectra of the same scatterer were obtained again. The ex-situ SEM images were obtained after disassembly of the cell. The dispersion interaction between gold nanorods and spheres were calculated using Derjaguin-approximation. The electric double layer interaction was calculated by finite-element method, implementing the nonlinear Poisson-Boltzmann equation. The interaction energies were given as total electrostatic free energy of the system. The input for the calculations regarding the surface charge densities were obtained from electrophoretic mobility measurements.

For the preparation of gold/silica Janus particles CTAB stabilized gold nanospheres were synthesized based on seed-mediated protocol. The stability of AuNPs in organic solvents can be effectively achieved by PEGylation of the nanoparticles using mPEG-SH. The PEGylated AuNPs dispersed in EtOH were transferred into 0.5 or 1 w/w% PS in toluene. This was spin-casted on a Si or glass substrate. Spin parameters were optimized so that the thickness of the resulting PS layer was smaller than the diameters of the AuNPs. The substrate with the partially masked gold particles was immersed in a silica growth solution. The concentration of the TEOS was set to be under the critical value of homogeneous nucleation. The feasibility of the preparation approach is demonstrated by the SEM images recorded after each consecutive preparation step. Optical properties of Janus particles with different morphology were investigated by single-particle scatterometry.

3 Results

3.1 Two-step surface modification of gold nanorods and site-specific assembly with citrate-stabilized gold nanospheres

A robust two-step surface modification procedure was applied to prepare patchy gold nanorods with spatially inhomogeneous surface-ligands, featuring positively charged molecules in the tip region and polymer molecules at the sides. The cysteamine addition resulted in a significant blueshift of the original longitudinal resonance peak (Figure 4a.). During surface modification the amount of the cysteamine molecules was optimized to achieve selective ligand exchange on the tips. Optical spectroscopic and electrokinetic measurements were performed for monitoring the modification process. While the LSPR shift provides information mainly about the refractive-index change at the rod tip, the electro-kinetic data characterizes the whole rod surface. In Figure 4b., the results of electrophoretic mobility measurements of the patchy particles are shown together with corresponding LSPR peak position as a function of cysteamine concentration. The results show, that the LSPR peak position reaches its final value
already around 1 mM cysteamine concentration, above which no further attachment takes place at the tips, while adsorption at the rod as a whole certainly proceeds up to 10 mM because of the increasing electrophoretic mobility. Consequently, tip-selective ligand exchange can be achieved below 1 mM cysteamine concentration.

Figure 4. a) The effect of the two-step surface modification of the nanorods on the extinction spectrum. b) Plot of the longitudinal peak position (left axis) and the measured with electrophoretic mobility values (right axis) of patchy particles as a function of cysteamine concentration.

The patchy surface modification provides a robust platform to assemble small (19 nm) negatively charged particles: due to electric double layer attraction, only two spheres at the opposite tips of the rod were bound, while the side attachment was prevented by the steric repulsion of PEG chains (Figure 5a.) As the sphere size increased apparent change of the assembly behaviour were observable: only a single sphere was attached at the side of the rods (Figure 5b.).

Figure 5. a) SEM image of the patchy nanorods assembled with 19 nm nanospheres and the corresponding extinction spectrum. b) Assembled structures using 40 nm gold nanospheres (SEM image and corresponding extinction spectrum).
Besides the relevance of sphere diameter, self-assembly experiments showed the effect of salt-concentration on the evolving structure. As the salt concentration is gradually increased, 2 spheres start to bind to the same rod at its opposite tips, then no assembly takes place (Figure 6.). This finding can be explained by the simultaneous reduction of effective range of both the repulsion between spheres and attraction between the rod tip and the sphere.

![Figure 6.: SEM images of the assembly experiments (60x16 nm AuNRs with 40nm AuNPs) performed at different salt concentrations.](image)

Calculated results related to colloidal interactions (i.e. electric double layer and dispersion interaction between the rod and sphere particles) shows the preference of nanosphere adsorption to the side region. Difference between interaction energies calculated for side and tip arrangements increases with sphere diameter, but in case of smaller particles (d ~ 20 nm) it is low enough to promote tip-selective assembly directed by PEG chains (Figure 7.).

![Figure 7. Difference between the electric double layer interaction energies calculated for the side (ΔG₂) and tip (ΔG₁) approach of 19 nm (brown line) and 54 nm (blue line) spherical particles.](image)
3.2 In situ investigation of rod/sphere heterodimers with single-particle scatterometry

Relying on the unique optical properties of the heterodimers composed of a patchy gold nanorod and nanosphere direct, in-situ information on the structure of the assembly can be obtained using single particle scattering spectroscopy combined with correlative electron microscopy investigations. This combined technique opens the possibility to correlate optical properties with relative position of the particles in the heterodimer. Ex-situ electron microscopy confirms that the spheres are located at the side of the rods and reveal their position distribution. Based on the position distribution, the majority (65%, first 3 categories in Figure 8b.) of the spheres can be found within 20 nm from the rod centre.

During in situ measurements, a blueshifted higher (H) and a redshifted lower (L) energy peak were appeared at around the initial longitudinal plasmon peak of the rod indicating the formation of a heterodimer (Figure 8a.). Based on the energy difference between the two peaks the spheres were attached to the side region already in the aqueous phase (Figure 8c.). During drying of the sample, there is no significant transformation of the heterodimer structure; no excessive displacement of the sphere is indicated (the effect of immersion type capillary forces and PEG chain collapse can be neglected or excluded).

![Figure 8](image)

*Figure 8. a) Typical scattering spectra measured in-situ in the liquid cell and the corresponding SEM images. The numbers indicate their respective relative displacement. b) Nanosphere position (relative displacement) distribution along the nanorod. c) Difference between the hybridized low-energy ($\lambda_L$) and high-energy ($\lambda_H$) plasmon peak wavelengths for individual heterodimers as a function of relative sphere displacement.*

3.3 Structural and optical properties of gold/silica Janus particles prepared by interfacial templating

A novel strategy for the preparation of gold nanoparticles partially covered by a silica cap have been developed. Due to the well-defined structure of the particles, and readily available well-established protocols for gold and silica surface modification, the prepared particles are excellent candidates for fundamental studies in programmed self-assembly of patchy nanoparticles at the nanoscale.
Symmetry breaking is achieved by embedding the gold nanoparticles in a polystyrene layer with well-defined thickness at an interface enabling partial exposure of the particle surface during wet-chemical silica shell growth. Precise control over the resulting particle geometry, that is, coverage and silica shell thickness can be achieved by fine-tuning the polystyrene film thickness and the silica shell growth time (Figure Hiba! A hivatkozási forrás nem található.).

Figure 9. SEM pictures showing the side-view of the “mushroom” particles. Different cap coverage was achieved by changing the thickness of the polystyrene layer: 50 nm (a), 33 nm (b) and 25 nm (c). Different shell thicknesses achieved by adjusting the contact time with the growth solution: 4 (d), 24 (e) and 72 hours (f).

Correlative electron microscopy and single particle scattering spectroscopy measurements underline the high precision and reproducibility of the method (Figure 10.). The presence of the shell induces significant redshift of the dipole resonance peak. The higher redshift observed for the 50% covered particle can be attributed to the higher coverage of the core particle (Figure 10g.). This finding was confirmed by the qualitative agreement between the experimental and theoretical shift. Furthermore, for a given particle type there is only a minor variation in the scattering spectrum, which underlines the size/shape homogeneity of these particles.

Figure 10. Side-view (a,b) and top-view (c,d) SEM images of the measured particles using 33 and 50 nm polystyrene film thicknesses. Dark field scattering optical images (e,f) of the same areas. Arrows
mark the individual particles used to obtain single particle scattering spectra. Averaged and
normalized single particle scattering spectra (g). The inset shows the magnified region around the
resonance peak for each individual spectrum.

4 List of theses

1. A robust two-step surface modification procedure was first applied to prepare patchy
gold nanorods with spatially inhomogeneous surface-ligands. The tip of the rods was
functionalized with positively charged cysteamine, and the side region was covered by
mPEG-SH ligands. These patchy particles were self-assembled with negatively charged,
citrate stabilized spherical particles. I show that the mPEG-SH coating on the side of
the rods (54×15nm) can effectively inhibit the side-attach of spheres with the diameter
of 20 nm, therefore tip-selective assembly was achieved. [1]

2. I confirmed that during self-assembly the bound-region of the spheres is varied with
their diameter. In case of spheres with the diameter of 40 nm, only a single particle is
attached at the side of the rods. The experiments were performed at different salt
concentrations, the results reveal the combined effect of colloid interactions on the self-
assembled structure: these are the electric double layer attraction between the tip region
and citrate stabilized spheres and the repulsive interaction between the spheres. [1]

3. In situ single particle scattering measurements of patchy nanorod (115×49 nm) /
nanosphere (54nm) heterodimers in the aqueous phase were performed. The results
indicate the formation of the heterodimer in the aqueous phase with the sphere already
attached to the side of the nanorod. Correlative electron microscopy investigations also
confirm the side-orientation of the spheres, the spatial arrangement of the heterodimers
formed in the aqueous phase is comparable with the ex situ observed results. [2]

4. Although attractive patches occur at tip-regions (115×49 nm rod), self-assembly
experiments performed at different salt concentrations supported by finite element
simulations applied to electric double-layer interaction show the preference of the side-
arranged larger spheres (54 nm). According to simulated results smaller spheres (19 nm)
have no preference in binding sites, hence PEG ligands present on the side region can
cause tip-selective assembly. [2]

5. A novel strategy was developed for the preparation of gold-silica Janus particles, where
gold nanoparticles partially covered by a silica cap. The interfacial preparation method
relies on partially embedding the gold particles in a polystyrene layer that masks the
immersed part of the gold particle during silica shell growth from an aqueous solution.
Precise control over the resulting particle geometry, that is coverage and silica shell
thickness, can be achieved by fine-tuning the polystyrene film thickness and the silica
shell growth time. [3] [4]

6. Single particle scatterometry reveals, that the presence of the shell induces a redshift in
the dipole resonant peak. The higher redshift can be attributed to the higher coverage of
the core particle. BEM simulations also indicate the correspondence between redshift
and coverage. The calculated results can be explained by the interaction between the
silica semishell and the near-field evolved on the core particle. [3]
5 Publications

5.1 Publications related to the theses:


5.2 Other publications:


5.3 Presentations:


[5] Pothorszky Szilárd, Zámbó Dániel, Dr. Deák Tamás, Dr. Deák András: Arany nanorészecskék irányított önszerveződése, Tavaszi Szél 2016.04.15. (oral presentation)