

# Discrete, Hierarchical Nanoparticle Assemblies and their Applications

by

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### Abstract

The design and fabrication of discrete and increasingly smaller structures is one of the main challenges of nanotechnology today. When it comes to precision in the (sub-) nanometre range, the commonly employed top-down fabrication techniques begin to show their limitations and also suffer from rapidly rising production costs. However, many applications would benefit from defined nanostructures with controlled shapes and dimensions. In order to produce such structures more cost-efficiently and with smaller features, bottom-up techniques may be employed to build the nano-devices from nano-scaled building blocks.

The main objective of this thesis was the investigation of an electrostatic nanoparticle assembly concept and its use for increasingly complex, sought after nanostructures. The assembly process was modelled with DLVO theory (by Derjaguin, Landau, Verwey and Overbeek) and the accuracy of those models was addressed in initial nanoparticle dimer assembly experiments. After that, the focus lay on the high-yield fabrication and detailed characterisation of hierarchical nanoparticle trimer structures that had been predicted to have outstanding plasmonic light focusing properties. Finally, a further extension of the assembly method to other particle materials and geometries was performed. This provided a cheap and simple toolset for complex, high-yield nanoparticle assemblies in dense arrays, which can be applied in fields such as plasmonics, (photo-) catalysis or microfluidics.

An electrostatic dimer assembly protocol developed by Dr. Y. Zheng was the starting point for the DLVO model and initial dimer assemblies. The influence of the different assembly parameters was assessed in theory and experiment, which led to the development of a size selective nanoparticle adsorption protocol. It allowed for the controlled adsorption of smaller nanoparticles from a bidisperse solution onto a prepared substrate (and thus nanoparticle sorting).

Following the study of the assembly concept, the protocol for the assembly of hierarchical nanoparticle trimers with increasing particle size was developed. This enabled the high-yield production of these plasmonic nanolenses over a large area, which was not possible before. These trimer assemblies were then characterised by UV-vis, cathodoluminescence and electron energy loss spectroscopy, which supported the theoretical predictions. Electrostatic eigenmode expansion was used to provide a more physically tangible interpretation of the numerical boundary element method results. Applied in surface enhanced Raman spectroscopy, the substrates showed molecular sensing capabilities superior to commercial ones.

The assembly technique was then transferred to different substrates, particle materials and particle shapes (which is essential for the applicability of the method to a very diverse field). The assembly of nanoparticles together with gold nanorods was investigated in greater detail again, as gold nanorods are often used as plasmonic nano-antennas for light. A high degree of control over the positioning of the nanoparticles with respect to the rods was achieved, which is required for such use cases. The easily scalable assembly processes developed in this PhD thesis pave the way for (but not limited to) future plasmonic and microfluidic applications.

### Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Julian Lloyd, June 2017

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## Acronyms and Abreviations

AFM	atomic force microscope
$\operatorname{AgNP}$	silver nanoparticle
APTES	(3-aminopropyl)triethoxysilane
AuNP	gold nanoparticle
BEM	boundary element method
BSPP	${\rm bis (p-sulfonate ophenyl) phenyl phosphine\ dihydrate\ dipotassium\ salt}$
$\mathbf{CL}$	cathodoluminescence
CTAB	cetyltrimethylammonium bromide
DDA	discrete dipole approximation
DLVO	Derjaguin, Landau, Verwey and Overbeek (theory)
DNA	deoxyribonucleic acid
EBL	electron beam lithography
eDDA	electron driven discrete dipole approximation
EELS	electron energy loss spectroscopy
EEM	electrostatic eigenmode method
FDTD	finite difference time domain method
FIB	focused ion beam
$\mathbf{GNR}$	gold nanorod
$\mathbf{LSPR}$	localised surface plasmon resonances
NP	nanoparticle
OD	optical density
$\mathbf{PS}$	polystyrene
PtNP	platinum nanoparticle
rcf	relative centrifugal force
SAM	self-assembled monolayer
$\mathbf{SEM}$	scanning electron microscope
SES	Stokes-Einstein-Sutherland (equation)
SERS	surface enhanced Raman spectroscopy
$\mathbf{SF}$	selectivity factor
SPR	surface plasmon resonance
STEM	scanning transmission electron microscope

- **STM** scanning tunnelling microscope
- **TEM** transmission electron microscope
- **TMAC** N,N,N-trimethyl-(11-mercaptoundecyl)ammonium chloride
- Tween20 polyoxyethylene (20) sorbitan monolaurate
- **UV** ultraviolet

"Ich geb' euch kurze Antworten, dann müsst ihr nicht so viel schreiben."

Lukas Podolski

## Chapter 1

## Introduction

In this first chapter, a few general ideas are presented to provide a motivation for the nanostructures that are topic of this study. Different applications and fabrication techniques are reviewed with respect to their benefits and drawbacks. Careful assessment of said advantages and disadvantages finally results in the thesis objective, which is split up into several milestones.

### 1.1 Motivation

Nanotechnology is a frequently used term which has permeated everyday life today. The National Nanotechnology Initiative defines it as "[...] science, engineering, and technology conducted at nanoscale, which is about 1 to 100 nanometers" and although it has only come to public awareness in recent decades, Richard Feynman is attributed to have started the discussion on basic concepts about nanofarbication. [1] While nanotechnology had actually been used for more than 100 years, people were not aware of it. It was Feynman who opened the discussion on manipulating materials with molecular and atomic precision in 1959. [1,2] In his lecture "There's plenty of room at the bottom" he formulated the idea of down-scaling current technology and he envisioned that one could use a scanning electron microscope (SEM) to write a scale of 1/25000 (a technique today known as electron beam lithography (EBL)). Feynman realised that such nanotechnology (not to be confused with miniaturisation), while being important for research ("[...] it might tell us much of great interest about strange phenomena [...]", would be much more important and ground-breaking for technical applications. [2]

Today it can be seen that he was quite right with his assessment, however it is also obvious that it takes time to develop such new technology. A crucial contribution to bring nanotechnology forward is given by the fabrication and imaging tools available. While SEM and transmission electron microscopy (TEM) used to image nanometre scale structures were available at that time, it was not until the invention of the scanning tunnelling microscope (STM) and atomic force microscope (AFM) in the 1980s by Binnig et al. that angstrom resolution imaging became possible. [3–5] But not only did that allow for high resolution imaging, it also enabled controlled, single atom manipulation, which in turn allowed for the fundamental investigation of nanoscale effects.

Nanotechnology has since experienced a wide integration in current technology, most prominently in integrated circuits with transistors of ever shrinking size. However, it is not only the small size (and therefore higher component density) that makes nanotechnology so interesting: Effects that are only available on this scale can be utilised for new applications. Among those are electron tunnelling (e.g used in a tunnel diode [6]) or the lotus effect which allows for the fabrication of inherently water repellent structures. Another effect that occurs in nano-sized metal structures are plasmonic effects that can be exploited in numerous fields. One thing that can be seen from these examples is that in order to bring a new technology forward, it is necessary to have a tool-set at hand that enables the easy fabrication of the structures or devices of interest. In the following section, the potential applications of nano-structures in plasmonic and other fields will be reviewed before a look is taken at the technology that is available to fabricate these devices.

### 1.2 Plasmonics

The first and most important field of applications for nano-sized metal structures (in the context of this thesis) is plasmonics. And while these effects can be used for various applications, they fundamentally all rely on plasmon resonances to occur, more specifically (localised) surface plasmon resonances ((L)SPR). A brief introduction to plasmonics will be given in the following, while an in depth review of the full theory can be found elsewhere in literature. [7–9]

When light impinges on a metal structure, the electrons in the metal oscillate as a result of the electric field of the light. The resonances of those oscillations are known as plasmon resonances. One does distinguish between propagating surface plasmons and local ones, as is illustrated in Figure 1.1. [8,10] In the first case (a), the SPR propagate over the metal surface as a charge density wave and decay. As the plasmon resonance conditions are strongly dependent on the dielectric environment at the metal interface, this effect has been used to probe this environment on the metal surface. [10–14]

#### **1.2.1** Single Particle Plasmonics

To observe LSPR, the metal structures need to be much smaller than the wavelength of the light (in at least one dimension). As can be seen in Figure 1.1b, this leads to coherent oscillations of the nanoparticles' electrons around the metal centre at a specific frequency. [8] This leads to a characteristic red colour of spherical gold nanoparticle colloids (Figure 1.1d). Early observation of this phenomenon were reported by Faraday in the 19th century. [9] To understand the origin of this scattering on a more fundamental basis, one has to solve the Maxwell equations. Gustav Mie has done that analytically for the case of spherical particles. [7] For the case of particles much smaller than the wavelength of the incident light, one can apply a third order power series approximation to obtain solutions that are simpler than Mie's expressions. [8]



Figure 1.1: Schematic illustrating the different effects of light impinging on a metal surface and metal nanoparticles: a) Periodic areas of opposite charges known as propagating surface plasmons. The electric field is indicated with the grey lines. (© 2007 Annual Reviews) [10]. b) Localised surface plasmons caused by the oscillating electric field of the incident light. Regions with high electric field densities occur at the poles of the nanoparticles perpendicular to the light path and along the polarisation axis. (© 2007 Annual Reviews) [10]. c) Calculated (Mie theory) electric field enhancement for a silver sphere with a 30 nm radius excited with light at the primary plasmon resonance (369 nm). (Reprinted with permission from [8]. ©2003 American Chemical Society). d) Colloidal solution of 40 nm gold nanoparticles with the characteristic red colour.

Equation 1.1 shows the expression of the optical extinction cross section  $\sigma_{ext}$  of a particle derived in that manner:

$$\sigma_{ext} = \frac{18\pi\varepsilon_m^{3/2}V}{\lambda} \frac{\mathrm{Im}(\varepsilon(\lambda))}{[\mathrm{Re}(\varepsilon(\lambda)) + 2\varepsilon_m]^2 + \mathrm{Im}(\varepsilon(\lambda))^2}$$
(1.1)

V is here the particle volume,  $\varepsilon_m$  the dielectric function of the surrounding medium and  $\varepsilon$  the complex (Re and Im) dielectric function of the particle. The resonance condition for Equation 1.1, which is known as Fröhlich resonance condition, [15] is given by Equation 1.2: [16]

$$\operatorname{Re}(\varepsilon(\lambda)) = -2\varepsilon_m \tag{1.2}$$

In combination with tabulated values of the dielectric function of the particle material (e.g. Johnson and Christy for gold or silver [17]) and the refractive index of the surrounding medium, one can determine the resonance frequency of a nanoparticle colloid.

However, this approximation is only valid for small, spherical particle sizes. For bigger particles (above about 20 nm for gold) higher order effects become more important and the resonance frequency becomes explicitly dependent on the size (as follows from full Mie theory). [7, 18, 19] These higher order effects generally lead to a shift of the resonance to larger wavelength (red shift).

While the understanding of the underlying physics is important and the effects described so far already offer potential use cases such as particle characterisation or molecular sensing, [9] it is another effect that has generated a great interest among researchers: local electric field enhancement that is a result of the plasmon resonances. An example is shown in Figure 1.1c, where the electric field enhancement  $|E|^2$  is calculated for a silver sphere which is illuminated with 369 nm light (its plasmon resonance wavelength). This results in hight field enhancements at the poles along the polarisation axis of the light. These field enhancements can be exploited for numerous applications (as will be shown further down) such as surface enhanced Raman spectroscopy (SERS) or photovoltaic devices.

### 1.2.2 Simple Coupled Systems

Using nanoparticles to achieve local field enhancements, people realised that when having aggregates of several particles on the surface, the local field enhancements seemed to be much higher. [20–23] Michaels et al. identified the junction of two (or more) aggregated particles as the important location for such high field enhancements.

Calculations show that the local field enhancement of nanoparticle dimers is indeed particularly high in the gap between the particles. [24–27] While the nature of these exceptionally high field enhancements had been discussed for some time, it is now widely accepted that a smaller gap between two nanoparticles in general yields a higher and more localised field enhancement. [28] When getting to narrow gaps below 0.5 nm, this general rule no longer holds due to quantum mechanical effects, however, this regime will be neglected here (as the structures presented in this thesis do not reach this regime). [29–31]



Figure 1.2: Plasmonic coupling illustrated with an energy level diagram. The energy levels are given for the isolated particles (black), a dimer with 2 nm gap (blue) and with a 10 nm gap (red). The corresponding spectra are given on the right. (Reprinted with permission from [32]. ©2011 American Chemical Society).

A simple and generally used model for the plasmons of such nanoparticle dimers is the plasmon hybridization model. [28,33,34] The concept is quite similar to the one of molecular orbitals, where the wave functions of the electrons in molecules are described as hybrid orbitals resulting from the interaction of atomic orbitals. [35] Within this model, the interactions of the single particle plasmons lead to the formation of bonding and antibonding plasmons that are shifted in energy (Figure 1.2). These energy shifts get larger with a decreasing interparticle gap, and while for larger gaps dipole interactions govern the dipolar plasmons, multipole oscillations affect the resonances for smaller gaps. [28] At this point, another related nomenclature will be introduced as well: the classification of the resonances in bright and dark modes. As can be seen in Figure 1.2, the dipole moments (indicated by "+" and "-") are aligned parallel for the bonding and antiparallel for the antibonding plasmons. As a result, the antibonding plasmon mode of the dimer does not have an overall dipole moment(assuming identical particles). Thus it cannot be (directly) excited by linear polarised light and is therefore called a dark mode. [36,37]

#### 1.2.3 Self-Similar Nanolenses

Developing the idea of coupled systems further, Li et al. published in 2003 an idea about a cascading plasmonic effect which enables self-similar chains of (metal) nanoparticles to be efficient nanolenses. [38] The geometry is rather simple and has since been a topic of numerous simulations (some examples are shown in Figure 1.3). The nanolenses consist of a chain of nanoparticles with decreasing particle size and also decreasing particle separation gap-size (i.e. they are self-similar). For the *i*th particle with radius  $R_i$ , the radius of the next particle given by:

$$R_{i+1} = \kappa R_i \tag{1.3}$$

 $\kappa$  is a constant with  $\kappa < 1$ . To achieve self-similarity the inter particle separation gap-size between 2 consecutive particles is given by:

$$d_{i+1,i+2} = \kappa d_{i,i+1} \tag{1.4}$$

Li et al. developed a multipole spectral expansion (MSE) method under the assumption that the nanolens structure is significantly smaller than the wavelength of the light and also applied a quasistatic approximation (Section 2.3.1, page 37). [39] The numeric calculations based on this method for a trimer system show a sharp longitudinal resonance that leads to local field enhancements  $\sim 10^3$  (Figure 1.3a–c). These enhancements are observed in the gap between the two smallest particles. Li et al. also note that exact self-similarity is not critical to obtain large field enhancements and show results for slight deviations in geometry.

After this initial study, others looked at similar systems. [40–44] Bidault et al. investigated self-similar gold nanoparticle trimer assemblies (particle sizes: 18, 8 and 5 nm) that they had fabricated by DNA-directed assembly (see from page 20 for details on the fabrication). Using generalised Mie theory (GMT), they were also able to show an exceptional high local field enhancement in the gap of the two smallest particles of the trimer (Figure 1.3e). Additionally, they compare the trimer to its partial dimers (i.e. a 18–8 nm and a 8–5 nm dimer) with the same gap sizes. They find that the local field enhancement



Figure 1.3: a) - c) Calculated local field enhancements for a self-similar silver nanosphere trimer for different excitation wavelength (as indicated). (© 2003 American Physical Society) [38]. d) A more recent simulation based on the discontinuous Galerkin time-domain method. Again, the highest field is found in the gap of the two smallest particles (field values are scaled to [-15, 15]; field shown for t = 15 fs). (© 2016 Elsevier B.V.) [40] e) Calculated field intensity enhancement map (logarithmic scale) for a self-similar gold nanoparticle arrangement as produced in experiment. (Reprinted with permission from [41]. ©2008 American Chemical Society).

of the bigger dimer is identical to the enhancement in the gap between the two bigger particles in the trimer. However, in the gap between the smaller particles of the trimer it's much higher when compared to the small dimer. This finding shows again, that it is not the smaller gap size between the smaller particles in a self-similar arrangement that causes the lensing effect, but rather the coupling of all three particles.

There are also studies which question the (superior) lensing effect of these self-similar structures. [45,46] As Pellegrini point out, they do not see a significant improvement over the field enhancement performance of conventional plasmonic dimers. [47] In their study they compare (among others) a symmetric dimer arrangement with a self-similar trimer. They correct for the particle sizes in order to adjust the total volume of each structure and allow a fairer comparison between the structures. They finally find comparable field enhancements for both structures, with a greater localisation for the self-similar lens. Due to the volume adjustments, this is however not in contradiction to the previous presented studies. As Bidault et al. point out: upon the attachment of the biggest particle to the trimer, the hotspot in the gap between the two smaller ones increases (which can prove very significant for a variety of applications, which will be discussed later). However, these seemingly contradicting results show that one needs experiments to test the different models against and to investigate the lensing effect under practical conditions.

#### 1.2.4 Non-spherical Particles for More Design Options

As Mie theory had shown, the plasmonic properties of a material can be altered by the nanoparticle sizes, which has been used in the examples above. However, not only the size, but also the shape of the particles is important for its plasmonic properties and this is where analytic methods rapidly reach their limits. The simplest shape change from a sphere is the elongation along one axis (or two axes), thus yielding an ellipsoid. This situation is described by Gans' theory. [48] For more complicated shapes such as triangles, rods, stars or more irregular ones, one generally resorts to numerical calculations (see next section). In the following, a few interesting properties of non-spherical particles and assemblies will be presented.

Similar to the aggregates of spherical particles, the use of non-spherical particles showed an improved performance in plasmonic sensing applications. [8] This led to the fabrication of numerous particle shapes. In particular, particles and structures with exceptional high local field enhancement and sensitivity to changes of the refractive indices at sharp tips were produced. [8,9,49] This field enhancement of the local field is stronger for a reduced tip radius.



Figure 1.4: a) Local electric field enhancement maps for a silver nanotriangle for an excitation at 770 nm with horizontally polarised light (side length: 100 nm, thickness: 16 nm) Red colours indicate high enhancement. (Reprinted with permission from [8]. O2003 American Chemical Society). b) Field enhancement map for a gold bipyramid for excitation at the resonance frequency (width: 30 nm, height: 83.4 nm, tip radius: 2 nm). [49] c) Same as b but for a gold nanorod (width: 14 nm, aspect ratio: 4.1). (O2007 American Physical Society) [49].

Figure 1.4 shows this filed enhancement for three different particle shapes: a triangle, a bipyramid and a nanorod. As can be seen especially well for the triangular particle, the intensity of the field enhancement is strongly dependant on the polarisation of the incident light as different plasmon modes are responsible for the focusing at different locations. In a particle with a large aspect ratio (like the rod) this would lead to different resonances visible in the absorption spectrum. In this case, one distinguishes between longitudinal (along the long axis) and transversal (along the short axis) plasmon modes. For nanorods, one is usually interested in the longitudinal mode, as it can easily be tuned by the length of the rod (while also having the higher field confinement). Using such nanoparticle shapes, one can design structures that use them as antennas for light harvesting. In that situation, the active medium (that needs the high electric field) would be put in the location with the high field, the plasmonic *hotspot*.

### 1.2.5 A Word on Different Calculation Methods

Before moving on and away from the plasmonic effect, a few different methods to calculate these properties shall be mentioned. For a more detailed discussion see e.g. Zhao et al. [50] As motivated above, it is possible to analytically solve the mathematical problem for simple structures like the spheres or ellipsoids. [7,48] This can be simplified for structures smaller than the wavelength of the incident light by applying the quasistatic approximation.

Other methods (for arbitrary structures) include the discrete dipole approximation (DDA). [51] In this method, the particle's volume and surroundings are modelled as a grid of polarizable elements. The response of those elements to an incident wave (or electron beam in eDDA) is then calculated assuming dipole coupling. Due to the long range of the dipole coupling and the 3-dimensional mesh, this method can prove quite computationally intensive at high grid densities.

Another widely applied method is the finite difference time domain method (FDTD). [52] Here, Faraday's and Ampere's law are solved using a grid again. Similar to the DDA, this results in intensive calculations again, especially when structures get large and high accuracy is required. [50]

A computationally less demanding method is the boundary element method. [53, 54] Here, the full Maxwell equations are reduced to a boundary problem. One therefore only has to build a mesh for the outline of the nanoparticles. Additionally, it is possible to vary the mesh size according to the location. One would use a denser mesh in areas where a large electric field gradient is expected and a coarser one elsewhere. More details on this method will be given in Chapter 3.

### 1.3 Applications

The just discussed, unique plasmonic properties of noble metal nanostructures are very useful for a wide range of applications. They are e.g. being incorporated in molecular sensors with single molecule sensitivity. This is mostly done by SERS fluorescence spectroscopy but also by refractive index sensing. [9,20,22,55,56] The nanostructures help here either to amplify the signal of the analyte (by focusing the electric field) or to detect the changes in the dielectric environment as outlined earlier. It has also been shown that the structures can, in such cases, not only act as the detector of molecules but also be used to trap the analytes in their plasmonic hotspot. [57] Some biomedical applications also utilise the plasmonic effects of nanoparticles e.g. by functionalisation of colloidal particles with capture molecules. [58,59] When in contact with the target molecule, the colloid would then experience a change in colour, fluorescent characteristics or colloidal stability.

Similarly, noble metal nanostructures are being used as antennas for light to enhance the performance of photovoltaic devices or photocatalytic reactions. [60–69] It is therefore not always the strong field enhancement that is utilised but also the so-called hot electrons. [70,71]

Another reason why nanoparticles or nanostructured surfaces are important is found outside the field of plasmonics: The fact that for any given volume, their surface area to volume ratio is much larger than of the same volume of bulk material. Nanoparticles are therefore quite suitable for catalytic applications in general, where a high surface area is needed. [72–75] Particularly interesting are the nanostructures where several co-catalysts in the form of nanoparticles are distributed to enhance different half reactions. [65,66,68,76]

For some applications, the nanoparticles are just used as intermediate step to facilitate the fabrication of other structures: In the quickly growing field of nanowire devices, gold nanoparticles can be used as seeds for the catalytic growth of silicon nanowires. [77, 78] As with many of the other potential applications, the ability to control the positioning of nanoparticles on the substrate is of vital importance.
# 1.4 Fabrication Approaches

While the previous sections were structured according to the nanoparticle arrangements and geometry, the fabrication techniques will be the determining factor in the subsequent section. First, top-down fabrications will be looked at and then different bottom-up approaches will be addressed.

### 1.4.1 Top-Down Techniques

The different top-down techniques will only be briefly discussed in this section as they are not the main focus of this project. As such, the experimental process will only be summarised, the focus will be on the fabrication results and characteristics as well as the applications of the so-produced structures.

#### Serial Fabrication Techniques

Serial fabrication techniques are generally characterised by some sort of probe that is used to fabricate the nanostructures by affecting the substrate at the position of the probe. To cover the whole substrate, the probe has to "write" the whole area in a serial fashion.

### Scanning Beam Lithography

Electron beam lithography (EBL) is a high resolution lithography technique where an electron beam is scanned over a substrate (much like SEM). The substrate is covered with a thin layer of electron sensitive resist like Poly(methyl methacrylate) (PMMA). Upon exposure to the electron beam, the polymer is cross-linked or degraded, depending on whether it's a negative or positive resist. After writing the structure into the resist, it can then be developed (thereby removing the not exposed or exposed regions of the film) and used for further etching or deposition steps. By using an electron beam, this technique can technically achieve a sub 5 nm resolution. [79]

Due to this high resolution and the convenient pattern designing process, EBL is commonly used to fabricate structures with special plasmonic properties. Liu et al. have shown how a sequential fabrication procedure of two EBL steps can be used to produce a gold nano-triangle with a palladium disc close to one tip. [80] The resulting structure can be seen in Figure 1.5a. In their work they detect the presence of hydrogen gas by a change in the plasmon resonance peak of the triangle-disk system. They thereby use the electric field focusing of the triangle at the tips (as seen in Figure 1.4a) and the dependence of



Figure 1.5: a) Top: The resonance peak position for the Au-triangle Pd-disk structure shown at the bottom when exposed to hydrogen gas (pressure given on the vertical axis). Bottom: SEM image of the structure with the Au-triangle in yellow and the Pd-disk in silver (scale bar is 50 nm). (© 2011 Nature Publishing Group) [80]. b) SEM image of a heterostructure with two gold nanorods and an indium tin oxide particle located in between them (scale bar: 200 nm). (© 2014 Nature Publishing Group) [81]. c) SEM image of Au pentamers fabricated by EBL (scale bar: 1µm, inset scale bar: 100 nm). (Reprinted with permission from [82]. (c) 2014 American Chemical Society). d) SEM image of an Au bowtie nanoantenna on a glass substrate fabricated by EBL (scale bar: 50 nm). (© 2016 Nature Publishing Group) [83]. e) SEM image of a bowtie aperture produced by focused ion beam milling (scale bar: 200 nm). (© 2016 Nature Publishing Group) [84] f) Photolithographically produced holes in a Ti mask on Si that was then used to etch holes in the Si substrate. (Reprinted with permission from [85]. (C) 2014 American Chemical Society). g) SEM image of the holes produced in f) after evaporation of gold form 2 different angles. (Reprinted with permission from [85]. C 2014 American Chemical Society). h)-j) Assembly principle for a polystyrene particle lithography mask with consecutive metal evaporation and particle removal. Such masks can be used to fabricate the nanotrimers shown schematically in (i) and in the SEM image in (j) (scale bar: 100 nm ). (Reprinted with permission from [86]. (C) 2014 American Chemical Society).

the resonance position on the local dielectric environment: palladium can absorb hydrogen within its crystal lattice and changes its dielectric properties upon doing so. [80, 87] In order to achieve large change in the resonance frequency, it was necessary to make the gap size as small as possible (the smallest measured one being 10 nm). With hydrogen being considered a future fuel, but also being highly explosive at low concentrations in air, reliable and sensitive hydrogen sensors become increasingly important.

Another example for a two step EBL fabrication for nano-sized heterostructure was shown by Aouani et al. [81] In their work they describe the fabrication of a structure with two gold nanorods and an indium tin oxide nanodisk between them (Figure 1.5b). With this system they were able to show high non-linear upconversion efficiencies, i.e. the light emission at a wavelength 3 times smaller than the incident light. Such systems are relevant in fields like bioimaging, drug delivery and photovoltaics. [64,81]

EBL is also commonly used for the fabrication of other (single material) plasmonic structures such as the ones discussed in Sections 1.2 and 1.3. Examples are here different shaped isolated particles and different dimer structures. [57, 82, 83, 88] The so produced structures generally aim to use the plasmonic field enhancement in small gaps for sensing applications or to facilitate chemical reactions. Examples are shown in Figure 1.5c and d.

Instead of using an electron beam to write structures in a resist, a focus ion beam (FIB) can be used to mill structures directly into the substrate. The intermediate developing step can therefore be avoided. Additionally, FIB allows for an additive processing such as localised chemical vapour deposition. [89]

### Scanning Probe Lithography

One does not have to use particle beams to write structures on a substrate: Sharp probes such as AFM tips have also been used to achieve this in several different ways. For the highest possible resolution, single atoms can be manipulated and individually moved in position as shown by IBM research. [90] A more practical method is dip-pen nanolithography, where an AFM tip is used to write structures with molecular ink, achieving a line width down to 30 nm. [91] In a reverse fashion, nanoshaving lithography uses an AFM tip to remove molecules of a self-assembled monolayer (SAM) in specific areas which allows line widths down to 15 nm. [92] Furthermore, AFM tips can be used to directly pattern a resist which can then use standard lithography techniques for further possessing. [93]

While those scanning beam lithography techniques offer an efficient and versatile fabrication technique, they suffer the inherent problem of all serial processing techniques: They cannot easily be upscaled to larger areas while keeping the processing time to a reasonable time frame. Additionally, they suffer from accuracy problems when small nanostructures with nano-sized gaps need to be fabricated.

# **Parallel Processing**

## Photolithography

The limited upscaling capabilities of the serial techniques due to the slow processing time are mitigated by parallel processing techniques such as photo lithography. It is conceptual similar to EBL, however, here a light sensitive resist is exposed by light through a mask with the desired structure. The resolution of photolithography is determined by three main factors: the wavelength of the utilised light ( $\lambda$ ), the numerical aperture (NA) of the projection lens and  $k_1$ , a process factor taking the mask into account. [94] The resolution is then calculated with the Rayleigh equation:

Resolution = 
$$k_1 \frac{\lambda}{\text{NA}}$$
. (1.5)

Equation 1.5 dictates that  $k_1$  and the wavelength need to be small and the NA large to achieve the highest possible resolution. NA values could be improved to 0.93 in air, the  $k_1$ has its limit at 0.25. [95,96] That leaves the wavelength as the last adjustable parameter and it can be seen that even in the extreme ultra violet regime, the resolution would not reach the small inter-particle gap sizes that are needed for the discussed structures. Even though the 14 nm technology (or its recent successor, the 10 nm technology) that is used to produce state of the art FinFET transistors seems to be able to push the resolution limit far down, this is not a widely applicable approach as the process and the design of the final structure are not easily customised and fabrication facilities are not easily available. [97]

While photolithography can hardly be used to directly define nanostructures with the small gaps that are needed for plasmonic applications, it can be used in combination with other techniques to achieve the desired resolution. One such method has been shown by Yang et al. for the fabrication of hetero-oligomers that were used for hydrogen sensing (Figure 1.5f). [85] In their work they use phase-shifting photolithography to define an array of holes in a Ti mask. After etching holes in the substrate, they then proceed to evaporate gold (or palladium) from different angles into those holes (Figure 1.5g). With that technique they achieved gap sizes of 10–20 nm and could show hydrogen sensing

capabilities, similar to the ones reported by Liu et al., without using EBL.

# Self-Assembled Masks

The so far presented techniques are (while being commonly used) rather expensive due to the sophisticated equipment needed to push them to their limits in both resolution and precision. There are other methods that mitigate these problems by using concepts that are more often found in bottom-up the techniques that will be discussed in the next section: The lithography mask is prepared by assembling polystyrene (PS) particles on the substrate. Those PS-particles have usually diameters in the range from a few 100 nanometres to several micrometers. Depending on the assembly technique and conditions, the resulting layers can be full monolayers or only an assembly of isolated particles. The second case can be seen in Figure 1.5h, where Syrenova et al. used electrostatic assembly to assemble the PS-particles on a charged layer. [86] In a subsequent step, another material can be deposited to form a film. After removing the PS-particles, the new film has holes at the particle positions and can be used for further etching and evaporation steps. Figure 1.5i illustrates how such a structure is used to fabricate a gold nanotrimer structure by evaporating gold from different angles. The resulting trimer shows a grainy structure that is typical for evaporated gold (Figure 1.5j).

# 1.4.2 Bottom-Up

A conceptually different fabrication approach is adopted with bottom-up techniques: rather than fabricating the final structures out of a bigger piece of material, the idea is to use small building blocks and manipulate them to form the final assembly. As such, there are two main tasks that need to be addressed: The synthesis of those building blocks and the strategies to assemble them in their final arrangement.

## **Particle Synthesis**

In Section 1.2.4 it was shown that the shape of individual nanoparticles greatly influences their plasmonic properties. In order to take advantage of that, the top-down techniques aim to define structures with the desired shapes. However, they often fail to produce flat surface sharp edges on the nanoscale. The grainy metal structures often found when using top-down fabricated structures therefore present a significant alteration of the ideal design (see e.g. Figure 1.5b and j).

These problems can be largely mitigated by the assembly of pre-synthesised particles.

By using different wet-chemical protocols, a large variety of nanocrystals can be synthesised. A selection of possible structures is shown in Figure 1.6. The morphologies range from simple spheres to rods, 2D polygons and 3D polyhedrons, branched structures and to more complex structures such as hollow particles. [98]



Figure 1.6: SEM and TEM images of a variety of different shaped nanoparticles with different plasmonic properties. 1 and 2: spherical, 3 - 9: rod-shaped, 10 - 16: 2D polygonal, 17 - 23: 3D polyhedral, 24 - 29: branched, 30 - 36: complex and 37 - 43: hollow structures. (© 2011 Nature Publishing Group) [98].

While other fabrication options are possible (e.g. ball milling), [99,100] only chemical synthesis will be addressed due to its advantages in control of morphology and crystallinity. [98] Generally the wet-chemical synthesis consists of two main processing steps: the initial seed formation and the consecutive growing of the particles. The example of gold nanoparticles will be used in the following paragraphs to outline the general synthesis process.

A widely used method to synthesise AuNPs is the citrate reduction method, where

sodium citrate is used to reduce terachlorauric acid in an aqueous solution. [101] Upon addition of the citrate to the terachlorauric acid solution, gold seeds form and particles start to grow until no further material is available. This itself can already be seen as a self-assembly process of atoms to form nanocrystals. By changing the amount of citrate added to the solution and also by adding other reducing agents (e.g. tannic acid), particle sizes between 3.6 and 200 nm have been demonstrated. [101–104] The larger nanoparticle sizes can be fabricated with high quality, when the seed fabrication and the growth process are separated in two distinct steps. [105, 106]

The separation of nucleation and growing step has an additional advantage: By adding surfactants like cetyltrimethylammonium bromide (CTAB) to the growing solution, the growth along certain crystal directions can be favoured. [107] CTAB alters the surface energy of the different facets of the seed particle, thereby allowing the non-symmetric growth with aspect ratios up to 30:1. [108]

When synthesising nanoparticle colloids, the colloidal stability and thus the prevention of uncontrolled agglomeration of nanoparticles due to van der Waals attraction is a concern. [109] One option to prevent aggregation (which is conveniently used when citrate is part of the synthesis process) is the electrostatic stabilisation. This can be achieved by adsorbing molecules with an absolute charge on the particle surface. This leads to a repulsive electrostatic interaction keeping the particles apart from each other. [101,103,109] Another way is known as steric stabilisation. Hereby the molecules adsorbed on the particle surface sterically hinder the agglomeration of the particles. [107,110] Those two methods can also be combined, as was done in some of the experiments presented in this thesis.

After preparation and stabilisation of the building blocks, one can then proceed with their assembly into functional structures. While the assembly techniques discussed in the following sections will mostly be focused on bottom-up techniques, some instances will still involve top-down methods.

### Capillary Assembly

A popular example for the combination of top-down and bottom-up fabrication techniques are capillary and convective assembly processes. Usually the goal here is the assembly of nanoparticles into lithographically defined structures. [111,112] The colloidal particles are guided into position by the capillary force when drying the substrate. This requires great control over the drying process. The results range from dense arrays of nanoparticles to single particle lines or even only one particle per template structure (Figure 1.7b). [113] When using non-spherical particles like nanorods, even control over the positioning of the rods is possible (Figures 1.7a, c and d). [114–116] But the templates for such assembly can also be prepared by simpler methods than EBL: Wrinkles on substrates have been shown to allow for similar control over convective assembly (Figure 1.7e). [117]



Figure 1.7: a) Schematic illustration of gold nanorods assembling vertically in a predefined pattern upon solvent drying with SEM image of the resulting assemblies (scale bar: 100 nm). (© 2012 Wiley-VCH) [115]. b) Holes with single particles assembled by capillary assembly (scale bar: 1 µm). (© 2007 Nature Publishing Group) [113]. c) and d) Nanorods aligned parallel and perpendicular to the assembly trenches (scale bar: 100 nm). (Reprinted with permission from [116]. © 2012 American Chemical Society e) Nanorod lines assembled into a wrinkled substrate. ([117]-Published by The Royal Society of Chemistry)

### Molecular Interaction Driven Assembly

## **DNA-Directed** Assembly

A different class of self-assembly methods that allows a great degree of freedom in very precise positioning of individual nanoparticles is the DNA (deoxyribonucleic acid) directed assembly. The basic idea here is to drive the assembly by using complementary single stranded DNA that would hybridise into the well known double-helix. [118, 119] This concept was first introduced by Alivisatos et al. and Mirkin et al. in 1996. [120, 121] Their works already presented two different possibilities of using the unique programmability of the DNA strands: Template assisted assembly and assembly by particle interactions only. Mirkin et al. used two batches of nanoparticles functionalised with different, noncomplementary DNA and formed larger structures by introducing linker-DNA strands. Those linkers had complementary sequences for the different DNA strands on each nanoparticle batch and could therefore link the particles by hybridising with their DNA coating. Alivisatos et al. also used nanoparticles with a single stranded DNA functionalised surface, however, the larger structures were formed by introducing a DNA template where the particle DNA could link to. This allowed for a precise placement of nanoparticles along a double-helix DNA template which they illustrated by dimer and trimer assemblies (Figure 1.8a and b).

This template concept was taken further, progressing from single DNA strands to whole 2D and 3D DNA structures. The fabrication of those templates is commonly known as DNA-origami. In DNA origami, DNA strands are sequenced in a way that causes them to fold into the desired sheets or 3D structures by hybridisation of their complementary parts (Figure 1.8c). [122] Single stranded "loose ends" are incorporated at the positions where the nanoparticles are intended to adsorb. [42,123–126] An example of such assemblies can be seen in Figure 1.8d, e and f.

Complex structures are also possible without DNA-origami: By e.g. using magnetic particles, a mix of different DNA strands on the particles or by limiting the DNA strands on the particles, sophisticated hierarchical assemblies have been realised (Figure 1.8g and h). [41,127–129] Additionally, the DNA assembly is often combined with top-down techniques. Hereby a substrate is functionalised with single stranded DNA to allow the adsorption of DNA-functionalised nanoparticles. [95,130]

### Other Molecular Interactions

The assembly of nanoparticles into defined aggregates or to specific locations on a template can also be driven by other molecules and functional groups as the following examples show. One to mention is the thiol chemistry that is also generally used to bind DNA strands to gold nanoparticles. [30, 134] The use of polymeric "glue" has also shown good results in both, template assisted (Figure 1.8i, j and k) and pure in solution assembly of hierarchical structures. [131, 135] Other, binary assemblies have been demonstrated using simple molecular cross-linkers. [136]



Figure 1.8: a) and b) TEM images of gold nanoparticles assembled along a DNA-template (scale bars: 10 nm). (© 1996 Nature Publishing Group) [120]. c) AFM image of a DNA scaffold fabricated by DNA origami (scale bar: 100 nm). (© 2006 Nature Publishing Group) [122]. d) Different sized nanoparticles individually assembled on a triangular DNA scaffold (scale bar: 40 nm). (Reprinted with permission from [42]. (c) 2010 American Chemical Society). e) Gold nanoparticle (small black particle) assembled on a DNA scaffold next to a virus capsid (scale bar: 40 nm). (Reprinted with permission from [124]. (C) 2014 American Chemical Society). f) Nanoparticle spirals assembled around a bundle of DNA strands (scale bar: 100 nm). (© 2012 Nature Publishing Group) [125]. g) Gold nanoparticle functionalised with a single strand of DNA each and consecutively assembled into nanotrimers (scale bar: 100 nm). (Reprinted with permission from [41]. (C) 2008 American Chemical Society). h) Nanoparticle multimers fabricated via DNA-directed assembly. (Reprinted with permission from [127]. (C) 2006 American Chemical Society). i) k) Assembly of gold nanoparticles on lithographically defined polymer brushes (scale bar j: 1 µm; scale bar k: 200 nm). (© 2015 Wiley-VCH) [131]. 1) TEM image of gold nanoparticles electrostatically assembled on a silica sphere (scale bar: 200 nm). (© 2002 Royal Society of Chemistry) [132]. m) TEM image of a spherical nanoparticle assembled on the tip or side of a gold nanorod by electrostatic interactions (scale bar: 20 nm). (Reprinted with permission from [133]. (c) 2010 American Chemical Society).

# **Electrostatic Assembly**

### In Solution Assembly

As has been mentioned above, a common way to stabilise the colloidal particles is by electrostatic interactions. Those electrostatic interactions can also be used to drive the controlled assembly of nanoparticles. [137] In a common in-solution assembly of different particles, positively and negatively charged particles would be present in solution and by adjusting experimental parameters (e.g. the ionic strength) arrangements such as the ones shown in Figure 1.81 and m can be achieved. [132, 133]

### Substrate Assisted

Similar to the other assembly techniques, the addition of a substrate adds another way of controlling the outcome. Such an approach for the assembly of nano-dimers has been presented by Zheng et al. [55] In this work, they develop a concept presented by Ma et al. further to a fully self-assembly driven process. [138] Ma et al. prepared a substrate with a stripe structure ( $\sim 100$  nm) carrying molecules with opposite charges (Figure 1.9a). When exposing this structure to a nanoparticle colloid of negatively charged AuNPs, they observed a funnelling potential allowing for a nanoparticle adsorption only on the positively charged stripes (Figure 1.9b). Notably, the adsorbed particles had a rather uniform nearest neighbour distance, as they repelled each other due to their negative surface charges.

Zheng et al. used this nanoparticle assembly concept on a positively charged substrate without a stripe structure. This resulted in a uniform distribution of negatively charged particles on a positively charged substrate. Similar to the stripe structure, those negatively charged AuNPs were expected to create a funnelling potential over the positive background charges. When adding positively charged particles in a second assembly step, those were guided towards the negatively charged ones forming dimers. Those dimers could be produced with a variety of particle sizes shown. Their high electric field enhancement in the interparticle gap was used for molecular sensing via SERS measurements.



Figure 1.9: a) Assembly concept: Stripes with alternating surface charge are used to direct the assembly of charged nanoparticles. [138] b) SEM image of the resulting nanoparticle assemblies with well separate particles. (Reprinted with permission from [138].  $\bigcirc$  2010 American Chemical Society). c)Assembly concept: Charged particles on a complementary charged substrate are used to direct the assembly of nanoparticle dimers. [55] d) SEM image of the resulting nanoparticle dimers (scale bar: 100 nm). ( $\bigcirc$  2014 Royal Society of Chemistry) [55]

# 1.5 Thesis Objective

Nano-sized structures offer promising possibilities for advanced future applications as demonstrated in the previous sections. Proof of concept studies have shown these capabilities with selected nano-structures. However, these studies often involve top-down fabrication techniques with their drawbacks, or use bottom-up fabrication techniques with low yields and poor scalability. This project therefore aims to explore the limits of a simple and easily scalable electrostatic assembly concept. It will be shown that no overly complex assembly strategies are necessary to fabricate structures that other techniques fail to produce at high yields. While the assembly and investigation of plasmonic structures such as the previously discussed trimer nanolenses was the main focus of this project, the applicability of the developed electrostatic assembly concept to other fields was investigated as well. To achieve these goals, several milestones had to be reached, as outlined below.

#### Fabrication of the building blocks

The method of choice was originally introduced by Zheng et al. and as it is purely based on electrostatic interactions of nanoparticles and also the substrate, those building blocks needed to be synthesised first. [55] Commercially available gold nanoparticles and substrate therefore needed to be conjugated with charge carrying molecules. Later on, this had to be transferred to other substrate and particle materials. Here, the initial aim was to achieve a high surface charge for the individual building blocks.

## Detailed understanding of the electrostatic assembly concept

While the fundamental concept had already been presented, a more detailed understanding was necessary to apply it for structures more advanced than nanoparticle dimers. Initial studies therefore had to focus on the understanding of the influence of all the assembly parameters on the final structures. A custom piece of written software code had to be developed to confirm the feasibility of different assembly ideas. The so developed concepts were then initially applied for size selective nanoparticle sorting and thereby the accuracy of the theory was tested. This could iteratively be done to develop a more accurate understanding of the process.

## Fabrication and characterisation of plasmonic trimer nanolenses

Once sufficient understanding of all parameters were established, an assembly strategy for structures comprising nanoparticles of three different sizes could be developed. This ultimately allowed for the fabrication of large amounts of self-similar plasmonic nanolens trimers for the first time.

These structures had to be investigated by optical and electron beam spectroscopy techniques. Due to the small size and the density of the assemblies, only techniques such as CL or EEL spectroscopy were suitable for the investigation of a single nanotrimer. Assembly therefore had to be accomplished on TEM girds as well. Boundary element method and electrostatic eigenmode method calculations were used to interpret the findings and draw conclusions on the lensing performance of the structures.

#### Expand the method to materials other than gold

To show the fundamental independence of method from the particle material and thereby showcasing its versatility, particle materials other than gold had to be used. This step mainly involved the surface functionalisation of the new nanoparticles to achieve a high surface charge.

### Using non-spherical particles

After using spherical nanoparticles of different materials for complex assemblies, the last step involved non-spherical particles: gold nanorods. The aim here was the control over the assembly position of a spherical particle with respect to the rod. To achieve this, the dimer or trimer forming process had to be accomplished for two different situations: Starting with a rod or starting with a spherical nanoparticle.

This completed the toolset of the electrostatic self-assembly: A simple concept to control nanoparticles of different shapes, sizes and materials in assemblies that to date have been hard to achieve with high yield.

# Chapter 2

# **Computational Methods**

The next sections will focus on the computational methods used in this project. Two different aspects are assessed from a theoretical point of view: Firstly, the electrostatic assembly process for the dimer and trimer structures and secondly the plasmonic properties of these structures.

constant	value [unit]
π	3.141592653589793
$k_B$	$1.3806488 \cdot 10^{-23} \; [\mathrm{J/K}]$
$N_A$	$6.02214129 \cdot 10^{23} \; [\mathrm{mol}^{-1}]$
e	$1.602176565 \cdot 10^{-19} \ [\mathrm{C}]$
$\varepsilon_0$	$8.854187817620389 \cdot 10^{-12} \; [\mathrm{F/m}]$
$\varepsilon_r$	78.55

Table 2.1: Table of physical constants as used for the calculations.

# 2.1 DLVO Theory for Electrostatic Assembly

In order to establish a good understanding of the electrostatic assembly process that was used for all experiments, it was necessary to have a good theoretical model. This would help to narrow down the parameter space and to develop new assembly protocols. A wide range of different relevant parameters can easily be screened by computational methods, which would not be possible (i.e. a large range of different surface charges) or very time consuming if done experimentally. While the calculations can never be 100% accurate (as some simplification had to be made), they help in understanding how different parameters affect the assembly outcome and therefore accelerate the experimental optimisation process. In the following sections, the general approach for these calculations is outlined after introducing the underlying theory.

# 2.1.1 The Idea of the DLVO Theory

The calculations are mainly based on fundamental theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO theory). [139,140] Using this theory, electrostatic interactions between charged surfaces in a liquid and their van der Waals interactions are accounted for by the specific interaction energies.

As a large contribution for the interaction energy is the result of surface charges on particles and substrates, the nomenclature needs to be clarified first. The main experimental parameter that was used to quantify the amount of charges on the surfaces is the zeta-potential ( $\zeta$ -potential). Figure 2.1 schematically illustrates a charged surface in an ion containing liquid. As can be seen, the (negative) surface charges lead to ion migration of the counter ions towards the surface. The layer with these counter ions (positive) is known as Stern-layer. Moving further away from the surface, the  $\zeta$ -potential is the potential at the shear plan, a region where the fluid is still considered stationary with respect to the surface. [141] This illustrates that the interactions of the ions in the close vicinity to



Figure 2.1: Schematic illustration of a negatively charged surface in an ion containing liquid. The ions distribution of the ions in the different zones is indicated by positive (green) and negative (red) ion species. The graph shows the potential for the different layers.

the surface and their response to the surface charges play an important role when looking at such a system. Hence the ionic strength of the liquid can be identified as a crucial parameter for the later experiments (besides the actual surface potential).

The second part of the DLVO theory focuses on the van der Waals interactions of the different surfaces. Those forces are mainly dependent on the surface materials (e.g. organic molecules on a gold surface) as will be shown in the next section.

# 2.1.2 DLVO Applied to Nanoparticle Assembly

DLVO theory has previously been applied to nanoparticle assemblies e.g. by Ma et al. or Zheng et al. and the following discussion is based on their work. [55, 138] The total interaction energy  $(E_{tot})$  can be described as a linear combination of all repulsive electrostatic interactions  $(E_{rep})$ , attractive electrostatic interactions  $(E_{att})$  and the van der Waals interactions  $(E_{VdW})$ :

$$E_{tot} = E_{rep} + E_{att} + E_{VdW} \tag{2.1}$$

The detailed composition of  $E_{rep}$ ,  $E_{att}$  and  $E_{VdW}$  depends on the system that is investigated. To keep it as general as possible, the interaction energies will be described for a few general cases in the following and then applied to the case of a nanoparticle dimer

assembly.

The electrostatic interaction energy for two spherical particles  $(E_{s,s})$  can be approximated as:

$$E_{s,s} = 4\pi\varepsilon_0\varepsilon_r \left(\frac{k_BT}{e}\right)^2 \frac{r_1 r_2}{d} Y_{eff}^s(1) Y_{eff}^s(2) exp(-\kappa(d - (r_1 + r_2))).$$
(2.2)

 $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  the relative permittivity of water,  $k_B$  the Boltzmann constant and e the elementary charge. Furthermore there are the radii of the nanoparticles  $r_1$  and  $r_2$ , the distance d between the particle centres, the scaled effective surface potentials  $Y_{eff}^s(1)$  and  $Y_{eff}^s(2)$  of the particles and the absolute temperature T.  $\kappa$  is the Debye-Hückel parameter of the surrounding solution which can be calculated according to the following equation:

$$\kappa = \left(\frac{2000N_A e^2 I}{\varepsilon_0 \varepsilon_r k_B T}\right)^{0.5},\tag{2.3}$$

where  $N_A$  is the Avogadro number and I the ionic strength of the solution.

An equation similar to Equation 2.2 can be derived for the electrostatic interaction of a sphere and a plane  $(E_{s,p})$ :

$$E_{s,p} = 4\pi\varepsilon_0\varepsilon_r \left(\frac{k_BT}{e}\right)^2 r_1 Y_{eff}^s Y_{eff}^p exp(-\kappa(d-r_1)), \qquad (2.4)$$

where  $Y_{eff}^p$  is the scaled effective surface potential of the plane substrate (other parameters as above).

The second part of the DLVO theory is the contribution of the van der Waals interactions. These are accounted for by the following equations for sphere to sphere  $(E_{VdW}^s)$ and sphere to plane interaction  $(E_{VdW}^p)$ :

$$E_{VdW}^{s} = -\frac{A_{H}}{6} \left( \frac{2r_{1}r_{2}}{2(r_{1}+r_{2})g+g^{2}} + \frac{2r_{1}r_{2}}{4r_{1}r_{2}+2(r_{1}+r_{2})g+g^{2}} \right) -\frac{A_{H}}{6} log \left( \frac{2(r_{1}+r_{2})g+g^{2}}{4r_{1}r_{2}+2(r_{1}+r_{2})g+g^{2}} \right),$$
(2.5)

$$E_{VdW}^{p} = -\frac{A_{sub}}{6} \left( \frac{r_{1}}{g} + \frac{r_{1}}{2r_{1} + g} + \log\left(\frac{g}{2r_{1} + g}\right) \right),$$
(2.6)

where  $A_H$  and  $A_{sub}$  are the appropriate Hamaker constants (the reported values of  $A_H = 2.5 \cdot 10^{-19}$  J and  $A_{sub} = 5.7 \cdot 10^{-20}$  J will be used throughout this work). [55,142,143] g denotes the gap between the two particles or the particle and substrate.

The above presented equations are fully suitable to calculate the total interaction energy for a given system of charged particles and a substrate. However, they needed to be linked to measurable parameters in order to be able to model the experimental situations. This has been done by Ohshima et al. and will be briefly summarised in the following paragraphs. [144–146]

For a binary electrolyte (such as the low concentrated NaCl solution that was used in the experiments), the effective surface potential  $\Psi_{eff}$  of a spherical particle can be written as (approximate solution of the non-linear Poisson-Boltzmann equations):

$$\Psi_{eff} = \frac{k_B T}{e} \frac{8 \tanh\left(\frac{e\Psi_0}{4k_B T}\right)}{1 + \left(1 - \frac{2\kappa r + 1}{(\kappa r + 1)^2} \tanh^2\left(\frac{e\Psi_0}{4k_B T}\right)\right)^{0.5}}.$$
(2.7)

 $\Psi_0$  is here the particle surface potential. Equation 2.7 yields the required scaled effective surface potential by:

$$Y_{eff}^s = \frac{e}{k_b T} \Psi_{eff}.$$
(2.8)

For the given experimental parameters (nanoparticles, low ionic strength),  $\Psi_0$  can be considered as given by the  $\zeta$ -potential as measured in experiment. [55, 141]

Equation 2.8 can be applied to a planar surface as well, as in that case  $r \to \infty$ :

$$Y_{eff}^p = 4 \, tanh\left(\frac{e\Psi_0}{4k_BT}\right). \tag{2.9}$$

With Equations 2.2, 2.4, 2.8 and 2.9, the electrostatic interaction energies for a given set of experimental parameters could now be calculated according to DLVO theory.

# 2.1.3 Software Implementation

For the actual calculations, shown above equations were implemented in a Python<sup>1</sup> module to provide the base for various assembly arrangements (*dlvolib.py*, see Appendix A.1 for full code). Throughout the custom designed program, the *numpy* and *matplotlib* libraries were used for highly accurate and fast calculations and 2D plotting. [147,148] In order to allow for an applicability to many different assembly scenarios, the library was set up in a modular way. Table 2.2 lists the different available methods (and their input parameters) that can be used to calculate the interactions of various particles and a surface in a liquid according to DLVO theory.

<sup>&</sup>lt;sup>1</sup>Python is a programming language: www.python.org

output	function name	input parameters
$Y^s_{eff}$	Y_eff_s	$T, \Psi_0, I, r$
$Y_{eff}^p$	Y_eff_p	$T, \Psi_0$
$E_{s,p}$	E_surface	$z, T, r, Y^s_{eff}, Y^p_{eff}, I, \varepsilon_r$
$E_{s,s}$	E_spheres	$z, l, T, r_1, r_2, Y^s_{eff}(1), Y^s_{eff}(2), I, \varepsilon_r$
$E^s_{VdW}$	E_VdW_s	$z, l, r_1, r_2, A_H$
$E_{VdW}^p$	E_VdW_p	$z, r, A_{sub}$

Table 2.2: The main functions provided in the *dlvolib* module to apply DLVO theory to a given assembly problem. "Input parameters" are the parameters that need to be provided to the function, "output" is the parameter that is calculated and returned by the function.

The main program would then use this library and allow the specification of all relevant assembly parameters, as there were: position and size of all involved particles, zetapotential of the particles and the substrate, temperature and ionic strength of the assembly solution. By combining the functions provided in *dlvolib*, it was possible to calculate  $E_{tot}$ for a specific nanoparticle arrangement. Figure 2.2 illustrates how the main program uses the experimental parameters to calculate  $E_{tot}$  for the situation shown in Section 1.4.2: The electrostatic dimer formation with a negatively charged AuNP (with radius  $r_1$ ) sitting on a positively charged surface and a positively charged AuNP (with radius  $r_2$ ) positioned above the surface at position (l, z) (see scheme in Figure 2.2).

The measured  $\zeta$ -potentials of particles and substrate are used to calculate the scaled effective potentials, which in turn can be used to calculate the electrostatic interaction energies. Finally  $E_{tot}$  can be calculated by adding the van der Waals energies. While these calculations only yield the total interaction energy for one set of parameters, the effects of the individual parameters (such as temperature or ionic strength) can now easily be investigated by repeating the calculations with adjusted parameter sets. This will be done and explained in detail in the following chapters.



Figure 2.2: Programmatic workflow to calculate the total interaction energy for a given set of parameters. The scheme in the centre illustrates the setup with the relevant parameters for each component (particles, substrate and surrounding fluid). Arrows indicate the stepwise calculation process of  $E_{tot}$  using the functions from Table 2.2 for the intermediate steps.

# 2.2 Considering the Maxwell-Boltzmann Distribution

The total interaction energy calculated with DLVO theory may present a repulsive barrier for different assembly pathways. In order to determine whether certain pathways are still viable assembly options, the energy available to the particles to overcome such an energy barrier needs to be considered. This will be highly relevant in Chapter 4, basics for the calculations will be discussed here.

Commonly, the average thermal (kinetic) energy of a particle at equilibrium for a defined temperature is calculated by: [149]

$$\langle E_{kin} \rangle = \frac{3}{2} k_B T \tag{2.10}$$

However, this is only an average, while this was often sufficient for an initial estimate for the feasibility of an assembly pathway, sometimes a more detailed distribution of energies was needed. In those cases the Maxwell-Boltzmann distribution for the energy was used<sup>2</sup>:

$$f(E,T) = 2\left(\frac{E}{\pi}\right)^{0.5} \left(\frac{1}{k_B T}\right)^{1.5} e^{\left(-\frac{E}{k_B T}\right)}$$
(2.11)

By integrating f for energies above a certain threshold, it was possible to estimate the percentage of particles that had an energy higher than this threshold energy. As it would in theory have been necessary to integrate  $E \to \infty$  (which is computational challenging), usually the percentage of the particles below a certain threshold was calculated (and later subtracted from 100%). Calculations were performed using Wolfram Alpha. [151]

 $<sup>^{2}</sup>$ While the use of this textbook Maxwell-Boltzmann distribution might be simplification of the real situation (e.g. rotational degrees of freedom were not considered, no adaptations to account for the nanoparticle geometry were made) it was considered sufficient to get the estimates needed for the interpretation of the experimental results. [150]

# 2.3 Modelling of the Optical Properties

In order to theoretically describe the plasmonic properties of the nanoparticle assemblies when illuminated by light (or an electron beam), the boundary element method (BEM) was used. [53, 152] The BEM approach was well suited for the nanoparticle structures at hand: There is a sharp interface between the particles and surrounding medium and those structures also have a smooth surface. That way, it was easy to discretise the surface with a suitable mesh (more in Section 2.3.2). Additionally, the BEM approach scales with the interface area but not with the volume (as opposed to FDTD or DDA methods, Section 1.2.5) which kept the computational effort at a level suitable for a desktop PC. [153] The calculations can offer a precise description of the optical properties, but sometimes fail to describe them in an intuitive way that helps in understanding the underlying physics. Therefore, an electrostatic eigenmode method (EEM) [15, 154] was used in conjunction with these BEM calculations to offer insight into the underlying physics. In the following section, the underlying concepts of the BEM and EEM calculations will be introduced, followed by an explanation of the computational realisation used in this project.

# 2.3.1 Boundary Element Method for Plasmonic Properties

The following introduction aims to summarise concepts behind the BEM approach as presented in papers by Garcia de Abajo et al., Hohenester et al. and Davis et al. [53, 54, 152, 155]

In general, to get insight on the plasmonic properties of a given structure, the main problem is to solve Maxwell's equations for that structure. There are different options to approach that problem, some approximations allowing for a significantly simplified calculation. Here, the most general and precise case will be discussed first: the exact solution of Maxwell's equations with retarded field calculations. In contrast to the quasistatic approximation discussed later (Section 2.3.1), the retarded solution accounts for the finite speed of light, which implies retardation effects for larger structures<sup>3</sup>. [156, 157]

<sup>&</sup>lt;sup>3</sup>The definition of "large" will be given in Section 2.3.1, when the quasistatic approximation is applied.

## Taking a Retarded Field into Account

As a starting point, Maxwell's equations are given by<sup>4</sup>: [149]

$$\nabla \cdot \boldsymbol{D} = 0, \tag{2.12}$$

$$\nabla \cdot \boldsymbol{D} = 4\pi\rho, \tag{2.13}$$

$$\nabla \times \boldsymbol{E} = ik\boldsymbol{B},\tag{2.14}$$

$$\nabla \times \boldsymbol{H} = \frac{4\pi}{c} \boldsymbol{j} - ik\boldsymbol{D}, \qquad (2.15)$$

with the electric displacement  $D = \varepsilon E$  and the magnetic flux density  $B = \mu H$ . Here are the dielectric function  $\varepsilon(\mathbf{r}, \omega)$  and the magnetic permeability<sup>5</sup>  $\mu(\mathbf{r}, \omega)$  (potentially) dependent on space and frequency. Using Equations 2.12 and 2.14 allows the definition of the electric (E) and magnetic (H) fields from the scalar and vector potentials  $\Phi$  and A:

$$\boldsymbol{E} = ik\boldsymbol{A} - \nabla\Phi, \qquad (2.16)$$

$$\boldsymbol{H} = \nabla \times \boldsymbol{A},\tag{2.17}$$

with

$$\nabla \cdot \boldsymbol{A} = ik\varepsilon \Phi. \tag{2.18}$$

Those potentials both fulfil the free Helmholtz equation with the following solutions: [53, 158]

$$\Phi(\mathbf{r}) = \Phi_{ext}(\mathbf{r}) + \oint_{V_p} G_p(\mathbf{r}, \mathbf{s}) \sigma_p(\mathbf{s}) d\mathbf{s}, \qquad (2.19)$$

$$\boldsymbol{A}(\boldsymbol{r}) = \boldsymbol{A}_{ext}(\boldsymbol{r}) + \oint_{V_p} G_p(\boldsymbol{r}, \boldsymbol{s}) \boldsymbol{h}_p(\boldsymbol{s}) d\boldsymbol{s}.$$
(2.20)

These solutions are valid for particles  $V_p$  with a homogeneous  $\varepsilon$  with sharp particle boundaries  $\partial V_p$  ( $\mathbf{r} \in V_p$ ).  $\sigma_p$  and  $\mathbf{h}_p$  here are surface charge and current distributions,  $\Phi_{ext}$  and  $\mathbf{A}_{ext}$  represent and external driving force (e.g. incident light).  $G_p$  is a Green function defined by:

$$(\nabla^2 + k_p^2)G_p(\boldsymbol{r}, \boldsymbol{r'}) = -4\pi\delta(\boldsymbol{r} - \boldsymbol{r'}), \qquad (2.21)$$

<sup>&</sup>lt;sup>4</sup>Gaussian units will be used in the following, unless otherwise stated.

 $<sup>{}^{5}\</sup>mu$  was set to one in the following.

$$G_p(\boldsymbol{r}, \boldsymbol{r'}) = \frac{e^{ik_p|\boldsymbol{r}-\boldsymbol{r'}|}}{|\boldsymbol{r}-\boldsymbol{r'}|}.$$
(2.22)

Equations 2.19 and 2.20 are then approximated with sums over discrete boundary elements (hence BEM). By using boundary conditions given by Maxwell's equations (continuity of the normal component of the dielectric displacement, the tangential component of the electric field and the magnetic field), a lengthy set of equations can be obtained that is solvable (which is generally implemented in a software). [53, 152, 158]

## **Quasistatic Approximation**

In the case of nanostructures much smaller than the wavelength of the incident light, quasistatic approximation can be used, as the retardation effects are negligible. Within the quasistatic approach, the electric field is described by the scalar potential only. Hence, Poisson or Laplace equations need to be solved, rather than the Helmholtz equation. One can readily write the solution as before:

$$\Phi(\mathbf{r}) = \Phi_{ext}(\mathbf{r}) + \oint_{V_p} G_p(\mathbf{r}, \mathbf{s}) \sigma_p(\mathbf{s}) d\mathbf{s}, \qquad (2.23)$$

with the electrostatic Green function:

$$\nabla^2 G_p(\boldsymbol{r}, \boldsymbol{r'}) = -4\pi\delta(\boldsymbol{r} - \boldsymbol{r'}), \qquad (2.24)$$

$$G_p(\boldsymbol{r}, \boldsymbol{r'}) = \frac{1}{|\boldsymbol{r} - \boldsymbol{r'}|}.$$
(2.25)

Note that Equation 2.25 can be obtained from Equation 2.22 for  $k\mathbf{r} \ll 1$ . Similar to the fully retarded case, the surface charge distribution can be determined by applying the boundary conditions given by Maxwell's equations and discretising the integral as a sum. Note that while the quasistatic approach only uses a scalar potential, the dielectric function is still frequency dependent (hence quasistatic). [152, 158] Finally, a matrix equation remains to be solved:

$$\Lambda \sigma_p + \sum_q \left(\frac{\partial G}{\partial n}\right)_{pq} \sigma_q = -\left(\frac{\partial \Phi_{ext}}{\partial n}\right)_p, \qquad (2.26)$$

with

$$\Lambda = 2\pi \frac{\varepsilon_2 + \varepsilon_1}{\varepsilon_2 - \varepsilon_1}.$$
(2.27)

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#### **Electrostatic Eigenmode Method**

The just discussed quasistatic approach is essentially equivalent to the EEM approach. It was therefore used to numerically calculate the surface charge distributions needed for the EEM discussions (Chapter 5). [55, 154, 158] The aim of the EEM approach is to describe the surface charge distribution as a sum of self-sustained eigenmodes. This is particularly appealing, as it allows for a more physically tangible description of the problem, as the eigenmodes can be interpreted as the different surface plasmons. The following introduction is based on the paper by Gómez et al. [15] Within EEM, the surface charge distribution of a particle q being excited at a certain wavelength  $\omega$  can be written as sum of eigenmodes of the particle:

$$\sigma_q(\mathbf{r}) = \sum_m a_q^m(\omega) \sigma_q^m(\mathbf{r}), \qquad (2.28)$$

where  $a_q^m$  are the excitation amplitudes for the different eigenmodes  $\sigma_q^m(\mathbf{r})$ . They fundamentally are a measure of the interaction strength of the incident light with the different eigenmodes. The dominant eigenmodes for a certain excitation can thereby easily be identified and allow for a physical interpretation (e.g. whether it's a mainly dipolar mode or with higher order excitation playing a significant role). The self-sustained surface charge distributions (i.e. eigenmodes) are here given by an eigenvalue equation:

$$\sigma_q^m(\mathbf{r}) = \frac{\gamma_q^m}{2\pi} \oint_{V_q} \sigma_q^m(\mathbf{s}) \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial n} d\mathbf{s}, \qquad (2.29)$$

with

$$\gamma_q^m = \frac{\varepsilon(\omega_q^m) - \varepsilon_b}{\varepsilon(\omega_q^m) + \varepsilon_b},\tag{2.30}$$

where  $\varepsilon_b$  is the dielectric constant of the surrounding medium and  $\varepsilon(\omega)$  the frequency dependent dielectric constant of the particle.

Equation 2.29 is essentially the same as Equation 2.26 (when discretised to a sum) with:

$$\gamma_q^m = -\frac{2\pi}{\Lambda_q^m}.\tag{2.31}$$

 $\gamma_q^m$  are the discrete eigenvalues corresponding to the different resonant modes  $\sigma_q^m$  in Equation 2.28. [154] Notably, for  $\gamma = 3$ , Equation 2.30 produces the Fröhlich equation (page 5), which predicts the resonance frequency of a spherical particle in Mie theory. Further down (Section 2.3.2) it will be shown that the corresponding eigenmode is the dominant dipolar

mode excited in a spherical nanoparticle by incident light.

While this EEM approach is already very useful for single structures, its full advantage can be seen when it comes to assemblies of several nanoparticles: The modes of the coupled system of nanoparticles is described as a superposition of the eigenmodes of the isolated particles. Hence the surface charge density of a coupled system of nanoparticles q can be written as:

$$\sigma(\mathbf{r}) = \sum_{q,m} \tilde{a}_q^m(\omega) \sigma_q^m(\mathbf{r}), \qquad (2.32)$$

with  $\tilde{a}_q^m(\omega)$  describing the coupling between the different modes m of the different particles q. These interactions can also be described by a coupling matrix  $\mathbb{C}$  that contains the coupling coefficients in its non-diagonal elements:

$$\tilde{a} = \mathbb{C}^{-1}a. \tag{2.33}$$

For the example of an assembly of two nanoparticles p and q this equation would take the form:

$$\begin{bmatrix} \tilde{a}_p \\ \tilde{a}_q \end{bmatrix} = \frac{1}{\Delta_2} \begin{bmatrix} 1 & C_{pq} \\ C_{qp} & 1 \end{bmatrix} \begin{bmatrix} a_p \\ a_q \end{bmatrix}, \qquad (2.34)$$

with  $\Delta_2 = 1 - C_{pq}C_{qp}$  the determinant of the coupling matrix.

For a chain of three particles (indices 1, 2 and 3) where only next neighbour coupling is taken into account, the coupling matrix takes the following form: [159]

$$\begin{bmatrix} \tilde{a}_1\\ \tilde{a}_2\\ \tilde{a}_3 \end{bmatrix} = \frac{1}{\Delta_3} \begin{bmatrix} 1 & C_{12} & 0\\ C_{21} & 1 & C_{23}\\ 0 & C_{32} & 1 \end{bmatrix} \begin{bmatrix} a_1\\ a_2\\ a_3 \end{bmatrix}, .$$
(2.35)

Equation 2.35 was used in Chapter 5 to discuss the results of nanoparticle trimers. Therefore, the coupling coefficients needed to be estimated. Coupling of the localised surface plasmons of two nanoparticles can be interpreted as a Coulomb-type interaction between their eigenmodes. [15] The strength of the interaction between two particles p and q can be described by their coupling coefficient: [15, 159, 160]

$$C_{pq} = -f_p(\omega)G_{pq} \tag{2.36}$$

 $f_p(\omega)$  is the frequency (of the incident light) dependant resonance factor. [159]  $G_{pq}$  is a

dimensionless factor accounting for the geometry of the particle assembly. [15, 159] In first approximation, this factor can be expressed as dipole-dipole coupling:

$$G_{pq} \propto d^{-3}[3(\boldsymbol{p}_p \cdot \hat{d})(\boldsymbol{p}_q \cdot \hat{d}) - (\boldsymbol{p}_p \cdot \boldsymbol{p}_q)], \qquad (2.37)$$

with  $p_{p,q}$  the dipole moments,  $\hat{d}$  the unit vector along interparticle axis and d the interparticle distance. As multiplication and dot product are commutative operations, it follows that  $G_{pq} = G_{qp}$ .

At this stage, all formulas and concepts that were used for the calculations of the plasmonic properties are presented. However, only a brief summary could be given here, much more detailed work can be found elsewhere in literature. [15, 154, 159] In the next section, the case of a single 30 nm AuNP will be used to illustrate the typical approach for the calculations.

# 2.3.2 Computational Procedure

The numerical BEM calculations were performed by using Matlab with the MNPBEM toolbox by Hohenester et al., which implements the above outlined approaches. [158] Code snippets for the different tasks described in the following paragraphs can be found in the Appendix A.2.

**Defining the Nanostructure** The first step of any calculation was the definition of the particle (or assembly) geometry and dielectric environment. Generally, a constant  $\varepsilon$  was assumed for the dielectric environment of the particles (the exact values are stated when the calculation results are shown in the subsequent chapters). Tabulated values from Johnson and Christy were used for the frequency dependent dielectric constant of gold. [17]

The particle geometry was generally defined by constructing a mesh grid with the highest possible grid density<sup>6</sup>. Figure 2.3 shows typical mesh grids for an isolated nanoparticle and a nanoparticle dimer. As can be seen, the mesh for the trimer was designed to have a high mesh density in the regions with the highest electric field. This was done to more accurately calculate the effects of these areas with a high field gradient. [15, 158]

<sup>&</sup>lt;sup>6</sup>The RAM of the employed computer was generally the limiting factor, the maximum grid point density was determined empirically for each setup.



Figure 2.3: a) Geometry of a spherical nanoparticle (yellow) with a uniform grid used for the BEM calculations (black lines). b) Similar grid as in a) for a dimer with a high mesh density in the gap region to achieve a high accuracy in this area of high electric field gradients. c) Surface charge distribution for nanoparticle excited along the vertical axis at its resonance frequency. Colours indicate the relative sign of the charges.

**Initialising the Solvers** After creating the particle (or several), the structure could be initialised. It then provides the geometry and dielectric information to the program for subsequent calculations. At this point, the decision about the calculation approach was made: Either using a quasistatic Eigenmode solver or the fully retarded solver, both with the advantages and restrictions as outlined before.

**Calculating the Spectra and Fields** Both solvers yield a BEM object that can also be used to calculate the surface charge distribution for a given excitation. This excitation can either be light with a defined polarisation or an electron beam. With this surface charge distribution, the absorbance at the given energy (wavelength) can be calculated. Through an iteration across numerous wavelengths, one can obtain a full absorption spectrum. Similarly, a spectrum of the scattered light can be calculated.

Additionally one can calculate the electric field distribution outside the nanostructure from this surface charge distribution. Using Greens function again, the induced fields (at any point) as a result of the charges on the nanoparticle surface can be calculated. [158, 161] It is therefore possible to find plasmonic hotspots (i.e. areas of high local field enhancement).

**Using the Eigenmodes** As shown in Figure 2.3c, the surface charge distribution may be superimposed on the particle geometry for a certain excitation. In the case of the sphere, this leads to the observation that the main excited mode is most likely a dipole mode along the vertical axis (as one would expect due to polarisation of the incident light

along this axis). However, for a more complicated structure, the dominant modes might not be obvious. In that case, the different eigenmodes can be extracted from the BEM object of the EEM solver. In combination with the calculated surface charge distribution, the excitation amplitudes can be retrieved (Equation 2.28). This is possible, as the full set of eigenmodes provides an orthogonal base for the surface charge distribution. [154] That way, the rather exact surface charge distribution obtained from the retarded BEM solver can be used and interpreted in terms of eigenmodes. An example for such a decomposition into different eigenmodes can be seen in Figure 2.4 for a spherical gold nanoparticle being excited with linear polarised light. The mode with the highest contribution is indeed a dipole mode as was already visible in Figure 2.3c. It can also be seen that modes with a negligible overall dipole moment are not excited by the linear polarised light (as indicate exemplary for one case).



Figure 2.4: The relative amplitudes (normalised to 1) for the different eigenmodes are plotted for the first 60 eigenmodes. The surface charge distribution is indicated for the dominant mode and an eigenmode with no overall dipole moment.

# Chapter 3

# **Experimental Methods**

This chapter will focus on the protocols for the preparation of the different building blocks and the basic assembly procedures. A list of chemicals and materials as well as a brief description of the equipment used is given.

# 3.1 Chemicals and Materials

Table 3.1 lists the chemicals used for the experiments. Unless otherwise stated later on, these chemicals were used without further purification.

All materials used throughout the project are listed in Table 3.2. It was found during the experiments that the citrate concentration used for the particle concentration differs between the two suppliers. As this affected the washing and functionalisation protocols, TedPella Inc. particles were used wherever possible.

Name	Supplier
(3-aminopropyl)triethoxysilane (APTES)	Sigma Aldrich
Bis(p-sulfonateophenyl)phenylphosphine dihydrate dipotassium salt (BSPP)	Sigma-Aldrich
Cetyltrimethylammonium bromide (CTAB)	GFS Chemicals
Deoxyribonucleic acid (DNA) monothiol (HS)-C6-T <sub>15</sub> -TTA TCA GGG TCA TAA	Fidelity Systems
Di-potassium hydrogen phosphate $(K_2HPO_4)$	Merck
Ethanol (EtOH), $99.96\%$	WVR
Hydrogen Peroxide ( $H_2O_2$ ), 30%	Sigma Aldrich
N,N,N-trimethyl-(11-mercaptoundecyl)ammonium chloride (TMAC)	ProChimia
Polyoxyethylene $(20)$ sorbitan monolaurate (Tween $20$ )	Sigma-Aldrich
Potassium dihydrogen orthophosphate $(KH_2PO_4)$	Merck
$\mathrm{SH-C_{11}H_{22}-(OCH_2CH_2)_6-OCH_2SO_3-Na^+}$ (TPS)	ProChimia
Sodium Chloride (NaCl)	Merck
Sulfuric acid $(H_2SO_4)$	J.T. Baker

Table 3.1: List of chemicals used.

# 3.2 Instrumental

The following section gives a brief overview of the instrumentation used for the experimental work. First, the instruments used for the fabrication will be listed and then the ones related to characterisation and analysis.

Name	Supplier
$100\mathrm{mm}$ p-type silicon wafer ${<}100{>}\mathrm{with}\ 110\mathrm{nm}\ \mathrm{thermal}\ \mathrm{oxide}$	University Wafer
$100 \mathrm{mm}$ borosilicate wafer	Plan Optik
$20\mathrm{nm}$ citrate stabilised AuNP	Ted Pella Inc.
$30\mathrm{nm}$ citrate stabilised AuNP	Ted Pella Inc.
$50\mathrm{nm}$ citrate stabilised AuNP	Ted Pella Inc.
$60\mathrm{nm}$ citrate stabilised AuNP	Ted Pella Inc.
$30\mathrm{nm}$ citrate stabilised PtNP	nanoComposix Inc.
$60\mathrm{nm}$ citrate stabilised AgNP	Ted Pella Inc.
$60\mathrm{nm}$ citrate stabilised AgNP	nanoComposix Inc.
Polybead Carboxylate $1.0 \ \mu m$ microspheres	Polysciences Inc.

Table 3.2: List of materials used.

# 3.2.1 Fabrication

**Centrifuges** An Eppendorf 5415R and an Eppendorf 5810R centrifuge was used for washing and concentrating the nanoparticle colloids. The centrifuges allowed for a fixed stable temperature during the centrifugation. Centrifugation times varied from 40 to 50 min, temperatures between 4 and 20 °C and speeds between 300 and 3100 rcf (relative centrifugal force). The exact parameters are detailed in the experimental protocols in Section 3.3.

**Thermomix** Eppendorf Thermomixer Comfort and Thermomixer C were used to shake particles during functionalisation at a set temperature and mixing speed. They were also used to maintain temperature between 10 and 35 °C during the assembly steps.

Water bath A Grant GD100 water bath was used for the 65 °C incubation assembly steps.

**Wafer Cutting** A Disco DAD321 automatic dicing saw was used to cut the wafers into  $4 \times 6 \text{ mm}, 3.5 \times 7 \text{ mm}$  or  $10 \times 20 \text{ mm}$  substrates that were used for the different experiments.

**Glovebox** An MBRAUN MB200 and an LC Technology Solutions Inc. LC-100 glovebox were used to store and handle oxygen or moisture sensitive chemicals. The required amounts of chemicals were transferred out of the glovebox before each experiment. **Balance** A Mettler-Toledo MS105U balance was used for measuring amounts of chemicals in the mg region. The balance has a repeatability of 0.04 mg.

**UV-Ozone** A SAMCO UV-1 UV-Ozone cleaner was used to clean the substrates after successful assembly and prepare them for SERS analyte loading. Cleaning was done with  $0.5 L/min O_2$  flow and UV-light enabled.

# 3.2.2 Characterisation and Analysis

UV-visible spectroscopy An Agilent Technologies Cary 60 UV-Vis spectrometer was used for all absorbance spectra measurements. Solution measurements were done using a Starna 50 µL quartz cuvette with a path length of 10 mm. UV-Vis spectra of solid substrates were taken by fixing a custom 3D-printed sample holder in the cuvette holder of the instrument. A baseline subtraction using either Milli-Q water or a functionalised substrate (without particles) was performed for all measurements.

**Zetapotential measurements** Particle  $\zeta$ -potentials to confirm successful DNA or TMAC modification were measured with a Malvern Zetasizer Nano ZS with disposable folded capillary cells. This instrument was also used to measure the hydrodynamic size of the particles, which gave additional information on the surface functionalisation.

An Anton Paar SurPASS was used to measure the  $\zeta$ -potentials of planar substrates. All measurements were performed with a 10 mM NaCl solution as electrolyte at neutral pH.

Scanning Electron Microscopy SEM imaging was done on three different systems: A FEI NovaNano 430 located at the Melbourne Centre for Nanofabrication and the Monash Centre for Electron Microscopy (MCEM) based FEI Nova NanoSEM 450 FEG-SEM and FEI Magellan 400 FEGS-EM systems.  $SiO_2/Si$  samples were investigated without further preparation or coating by fixing them on the SEM stub with carbon tape. Glass substrates where coated with a 5 nm Pt layer.

**Transmission Electron Microscopy** TEM investigations were done using a FEI Tecnai G2 T20 TWIN TEM and the FEI Titan<sup>3</sup> 80-300 FEG-TEM based at the MCEM. The T20 operated at 200 kV acceleration voltage and permits a point resolution of 2.4 Å. See next paragraph for further details on the Titan.

Electron Energy Loss Spectroscopy STEM imaging and EELS mapping were carried out on a double-Cs corrected FEI Titan<sup>3</sup> 80-300 S/TEM equipped with a Gatan Image Filter (GIF Tridiem 863P), operating at 80 kV and with a standard Schottky field emission gun (FEG) without a monochromator. The electron gun lens setting was adjusted to reduce the beam current, so that the EELS energy resolution could be improved to  $\sim 0.5 \text{ eV}$  (from 0.8-0.9 eV for a Schottky FEG) as measured from the FWHM of the zero-loss peak. A  $\sim 17 \text{ mrad}$  convergence angle was used to yield a  $\sim 2 \text{ Å}$  diameter electron beam, and a  $\sim$ 16 mrad collection angle was used for EELS mapping. The EELS map in Section 5.5.3 was taken with 35 ms acquisition time for each pixel and 1.8 nm step size. Principal component analysis and non-negative matrix factorization were employed separately to disentangle the signal (different plasmon modes and zero-loss peak). [162] These measurements were performed by Dr. Ye Zhu.

**Cathodoluminescence Spectroscopy** CL measurements were conducted with a Delmic SPARC Cathodoluinecence System mounted on an FEI Nova NanoSEM 450. An Andor Shamrock 303i spectrometer with a 150 l/mm grating and an Andor iVac spectral camera (2000 × 256) were employed to collect the spectra. A Jacobian transformation  $(hc/E^2)$  was applied to the CL data to convert to intensity per unit energy. [163]

**Atomic Force Microscopy** A PicoPlus bench-top AFM (Molecular Imaging) was used for surface topography measurements with MikroMash NSC15/AlBS probes. AFM maps were processed using the WSxM software. [164]

Surface Enhanced Raman Spectroscopy A Renishaw RM 200 confocal-raman system with NIR diode laser (782 nm) was used for the SERS measurements. The laser was fine focused with a  $\times 50$  objective to a spot size of  $\sim 4 \text{ mm}^2$ . The acquisition time was 10 s for all spectra, the range was kept constant. Laser power measurements were not performed, as the SERS data was only used to compare the performance of different substrates to each other and not for field intensity calculations.

# 3.3 Building Blocks

The following section is dedicated to the fabrication, functionalisation and characterisation of the building blocks: The different nanoparticles and the substrates. Figures 3.1a and b



show photos of the initial materials that were used throughout the experiments.

Figure 3.1: Photos of the different materials used for the assembly experiments. a) Nanoparticle colloids (from left): Gold nanorods (as prepared), diluted GNRs showing the characteristic blue colour, 30 nm platinum nanoparticles, 60 nm silver nanoparticles, 20 nm gold nanoparticles and 60 nm gold nanoparticles. b)  $SiO_2/Si$  wafer diced into  $4 \times 6$  mm pieces. c) Typical centrifugation result of an AuNP colloid tube with settled AuNPs at the bottom and 0.9 mL supernatant extracted. d)  $SiO_2/Si$  and glass substrates with nanoparticle assemblies on them in a vertical drying position.

# 3.3.1 DNA Conjugated AuNPs

Thiol-gold chemistry was used to bind single stranded DNA with a thiol functional group to the gold nanoparticles. As can be seen in Figure 3.2a, the sugar-phosphate backbone that connects the different bases is negatively charged. This charge (besides some steric hindrance) is used to stabilise the AuNPs in the colloidal solution once the citrate is removed and also later for the electrostatic assembly.

### Functionalisation

A protocol developed by Dr. Y. Zheng was used for the DNA modification of 30 nm AuNPs. [55] In a typical experiment, 1 mL of citrate stabilised AuNPs (OD = 1) were concentrated to 0.1 mL by centrifugation at 1500 rcf followed by extraction of 0.9 mL supernatant. The AuNPs were then redispersed by vortexing. Additions of the following chemicals were done under continuous vortexting. 5 µL of a 2% Tween 20 solution for additional colloidal stability for the subsequent citrate - DNA exchange process. [165] 30 µL of a 0.1 M phosphate buffer solution to stabilise the pH at 7 throughout the functionalisation process. 50 µL of a 2 M NaCl solution to increase the packing density of the subsequently added DNA strands. The NaCl helped to shield the charges on the phosphate backbone of the DNA strands. 20 µL of a 100 mM solution of single stranded DNA with a thiol
functional group was added before finally adding 5 µL of a 100 mM BSPP solution. The BSPP helped to reduce the disulfide bonds of the thiolated DNA (which was capped with a protecting mercaptohexanol group). [166] The mix was then left for incubation over night in a thermomixer at 20 °C and continuous shaking at 700 rpm.

In order to remove excess chemicals from the colloidal solution after the functionalisation step, a stepwise washing program was applied to the solution. A washing step consisted of redispersing the colloid to 1 mL with Milli-Q water, centrifugation of the solution at a given speed and temperature for 45 min and subsequent extraction of 0.9 mL supernatant (see Figure 3.1c). Details for the individual washing steps are listed in Table 3.3. The final solution of washed 30 nm AuNPs was redispersed to 1 mL. For the DNA

Size	speed [rcf]					temperature	$\operatorname{time}$
[nm]	run 1	$\operatorname{run} 2$	run 3	run 4	$\operatorname{run}5$	[°C]	[min]
30	1500	1800	2100	2500	2900	10	45
20	2100	2400	2700	3100	-	10	45

Table 3.3: Parameters for the particle washing (by centrifugation) after the surface modification with DNA.

modification of 20 nm AuNPs, the protocol had to be slightly adapted. The particle density of the initial colloid was adjusted to  $OD = \sim 0.65$  to account for the higher particle concentration of 20 nm AuNPs at a given optical density. The final washed colloid was redispersed to  $250 \,\mu$ L.

Functionalised particle colloids were stored in the fridge at 4 °C until use. While the final colloids were stable for several weeks, a fresh solution was used for each experiment to avoid any complication due to different storage times.

#### Characterisation

In order to determine the particle concentration after functionalisation and washing process, UV-vis spectra were routinely taken. As discussed in the introduction, the excitation of plasmons in the AuNPs leads to a characteristic resonance peak in the absorption spectrum of the colloids. The optical density at this peak position is commonly used to determine the particle concentration. It is therefore used as a convenient quantisation of the particle density of a colloid for a given particle size. Typical UV-vis spectra for DNA functionalised 20 and 30 nm AuNP solution are shown in Figure 3.2c. The optical density



Figure 3.2: a) Molecular structure of a DNA sequence consisting of the four different DNA nucleotides. Negative partical charges are distributed along the phosphate backbone of the DNA. b) Molecular structure of Thiol-PEG-sulfonate which was used as an alternative for the DNA functionalisation. c) UV-vis spectra of citrate stabilised 20 (blue) and 30 nm (green) AuNPs. The relevant part of a spectrum of the DNA functionalised 30 nm AuNPs is given in orange.

was then used to calculate the dilution factor to reach the final density for the assembly process.

A Malvern Zetasizer was used to determine the  $\zeta$ -potential of the nanoparticles. This allowed for accurate calculations of the electrostatic assembly process and also for and estimation of the quality of the surface functionalisation. The  $\zeta$ -potential for the DNA functionalised AuNPs was typically  $-69 \pm 5 \text{ mV}$ . Problems with the surface functionalisation of the particles could be detected by a low  $\zeta$ -potential or a large scatter in the measured signal.

#### 3.3.2 TPS Conjugated AuNPs

Alternatively, TPS (see Table 3.1 and Figure 3.2b) was used to convey a negative surface charge to the 30 nm AuNPs with a thiol-gold bond. The functionalisation protocol was almost identical to the one for DNA besides a few steps that will now be outlined. Up

to the addition of the NaCl solution, the procedures were the same. However, instead of DNA or BSPP,  $10 \,\mu\text{L}$  of a 1.66 mM TPS solution was added. From here on, the protocol followed the procedure as outlined above for the DNA functionalisation. The resulting  $\zeta$ -potentials were similar as well ( $-70 \pm 5 \,\text{mV}$ ).

#### 3.3.3 TMAC Conjugated AuNPs

#### Functionalisation

To convey a positive surface charge to the nanoparticles, they were functionalised with TMAC (see Table 3.1 and Figure 3.3a). In case of the 50 and 60 nm AuNPs, this was done by using protocols developed by Dr. Y. Zheng, in all other cases these protocols needed to be adapted. [55]

The TMAC functionalisation of the (initially citrate stabilised) AuNPs resulted in a surface charge inversion. To avoid particle agglomeration during this process, the amount of citrate was reduced by a washing step similar to the first washing step after functionalisation (Table 3.5). The starting solution was in all cases 1 mL of colloid (OD = 1.0). After the initial washing step, the colloid was concentrated to 100  $\mu$ L by centrifuging and extracting 0.9 mL supernatant.



Figure 3.3: a) Molecular structure of the TMAC molecule used to confine positive charges to the AuNPs. b) UV-vis spectra of the resonance regions of TMAC functionalised 20 and 50 nm AuNPs. The colloids were diluted to allow for reasonable accurate UV-vis measurements.

Under continuous vortexing, a set amount of a TMAC solution according to Table 3.4 and  $100 \,\mu\text{L}$  of a 6 mM CTAB solution (see Table 3.1) were added to the so produced colloid.

The CTAB helps to provide steric stabilisation during the charge exchange process and prevents agglomeration of particles as the TMAC replaces the negatively charged citrate molecules. [167] The solution was then incubated overnight in a thermomixer at 20 °C and 700 rpm. Excess chemicals were then removed by a washing protocol similar to the one for

Material	Size [nm]	Volume $\left[\mu L\right]$	concentration [mM]
Au	60	2.0	12
Au	50	2.4	12
Au	20	25	24
Ag	60	2.5	12
$\operatorname{Pt}$	30	12.6	12
Au	$20 \times 50$	8.0	24

Table 3.4: Volume and concentration of the TMAC solution added for the functionalisation of the different nanoparticle colloids. Apart from the bottom line (the gold nanorods) all particles were spherical particles.

the DNA-AuNPs with the details of the centrifugation steps given in Table 3.5. Note that in contrast to the DNA functionalisation, the centrifugation speed was decreased for the consecutive washing cycles. This was necessary to prevent agglomeration as the CTAB got washed out of the solution.

Material	Size	centrifugation speed [rcf]					temperature	time
	[nm]	run 1	run 2	run 3	run 4	run $5$	[°C]	[min]
Au	60	1000	400	300	300	300	10	40
Au	50	1000	800	700	500	400	10	40
Au	20	1800	1600	1450	1450	-	20	45
Ag	60	1000	800	600	500	-	10	40
$\operatorname{Pt}$	30	1000	950	850	750	750	10	40
Au	$20 \times 50$	1600	1450	1300	1150	-	10	40

Table 3.5: Parameters for the particle washing (by centrifugation) after the surface modification with TMAC.

#### Characterisation

The resulting colloids were routinely characterised by UV-vis and  $\zeta$ -potential measurements to confirm the final optical density and the particle surface charge. The  $\zeta$ -potential of the 60 nm AuNPs was typically  $+55\pm5$  mV, and  $+60\pm5$  mV for the 50 and 20 nm ones.

#### 3.3.4 TMAC Conjugated AgNPs

The optimisation of the functionalisation for particles other than the 50 and 60 nm AuNPs was done in an iterative process in two separate steps: First a large excess of TMAC was provided in the functionalisation solution to optimise the centrifugation conditions. Nanoparticle agglomerates or not completely settled colloids were indicators for suboptimal conditions. In a second step, the TMAC concentration was adjusted to yield a stable zeta potential for the functionalised particles.

An initial colloidal density of OD = 2.2 (at ~ 430 nm) was used for the functionalisation of the 60 nm silver nanoparticles (see Figure 3.4 for UV-vis spectrum). After the same washing step as for the 60 nm AuNPs and concentration to 0.1 mL, 2.5 µL of 12 mM TMAC solution and and 100 µL of a 6 mM CTAB solution were added to the colloid. Consecutive incubation and washing steps were similar to the AuNPs (details in Table 3.5). The functionalised AgNPs showed a lower  $\zeta$ -potential of  $+45 \pm 5$  mV, which indicated a lower TMAC loading on the individual particles.



Figure 3.4: UV-vis absortion spectrum of the 60 nm AgNP colloid. The colloid was diluted for the UV-vis measurements.

#### 3.3.5 TMAC Conjugated PtNPs

Similarly to silver, the 30 nm platinum particle used an adjusted protocol. The starting solution was prepared by diluting 0.5 mL of the NanoXact<sup>TM</sup> citrate stabilised PtNPs with

Milli-Q water to 1 mL. The same pre-functionalisation washing step as for AgNPs was applied, followed by the addition of 12.6 mL of 12 mM TMAC solution and 100 µL of a 6 mM CTAB solution. After overnight incubation, they were washed according to the protocol outlined in Table 3.5. The resulting particles show a  $\zeta$ -potential of  $+50 \pm 5$  mV.

#### 3.3.6 TMAC Conjugated GNRs

The functionalisation of the gold nanorods followed a similar protocol, however, no charge inversion had to be performed as the GNRs were already positively charged, stabilised in a CTAB solution. The GNRs were provided by Dr T. Thai. [114] 0.1 mL of the provided nanorods were washed once with Milli-Q. The optical density of the solution was 10.5 (at 644 nm), a full UV-vis spectrum of the initial solution is shown in Figure 3.5 along with a TEM image. As can be seen, there are some non rod-shaped impurities and also some rods of different sizes present in the colloid. However, this will not be highly relevant for later experiments, as those impurities can can be accounted for in the statistics.

TMAC (according to Table 3.4) and 100 µL 6 mM CTAB were added before an overnight incubation as above. The washing by means of centrifugation was performed according to Table 3.5. A UV-vis spectrum of the functionalised colloid can be seen in Figure 3.5a (green).



Figure 3.5: a) UV-vis spectra of the initial CTAB stabilised GNR colloid (orange) and the TMAC functionalised GNRs (green; both diluted for the UV-vis measurements). b) TEM image of the initial GNR colloid drop-casted on a TEM grid. (scale bar: 100 nm)

### 3.3.7 Substrate Preparation

Different substrates with and without surface functionalisation were used throughout the experiments, however, the fabrication process was mostly the same for all of them. Silicon

wafers with a 110 nm layer of thermally grown silica were mostly used, unless transparent substrates were needed (borosilica substrates were used in that case). The idea of the silica layer on the silicon substrates was to allow for an easy transfer of the assembly protocol to the glass substrates.

For the usual experiments, the wafers were cut into  $4 \times 6 \text{ mm}$  pieces with a dicing saw. For the  $\zeta$ -potential measurements, those sizes were changed to  $10 \times 20 \text{ mm}$ . The so produced pieces were then individually marked with a diamond pen and subsequently cleaned with (phosphate free) detergent by wiping them with a detergent solution soaked cotton ball. After rinsing with Milli-Q water, the substrates were then immersed 1 h in a piranha solution (3 parts H<sub>2</sub>SO<sub>4</sub>, 1 part H<sub>2</sub>O<sub>2</sub>). The main purpose of the piranha treatment was to clean the substrates of any remaining organic residues that would influence the subsequent functionalisation and assembly steps. Without this cleaning step, assembly was still possible however, the assemblies had more defects and were less uniform. Following the piranha treatment, they were washed with Milli-Q water by filling, shaking and emptying the beaker with the substrates 5 times. Finally, the substrates were dried by blowing them with a stream of nitrogen.

At this stage, the substrates showed a negative  $\zeta$ -potential of  $\sim -36 \,\mathrm{mV}$  at neutral pH, which was expected. [168] If a negatively charged substrate was needed for the assembly process, the preparation steps were finished at this stage. However, for most assembly procedures in the following chapters, a positively charged substrate was needed. The substrates were therefore immersed in a EtOH/APTES/Milli-Q (9.5 mL/0.2 mL/0.3 mL) solution to assemble a monolayer of APTES (see Table 3.1) on substrate via a silanisation reaction. [55, 169] After a 1 h incubation, the substrates were washed 3 times with EtOH and then dried under a stream of nitrogen. Finally, the substrates were baked for 20 min at 110 °C in the oven to stabilise the silane bonds. [170–173] While for the SiO<sub>2</sub>/Si substrates a 10 min baking was enough (and that was used for the early experiments) the functionalisation on the glass substrates required a longer baking. Both types of substrates showed a  $\zeta$ -potential of  $\sim +20 \,\mathrm{mV}$  after the functionalisation, which is consistent with the literature. [55, 169, 170]

# 3.4 Assembly

In the following chapters different assembly steps will be performed, however, the general procedures are mostly the same for all of them. In a typical assembly step, 0.2 mL of the desired particle colloid (at a specified concentration) was put in a 1.7 mL centrifuge tube. After the substrate was added, the closed tube was put to incubate at a certain temperature for a given time either in the thermomixer (no shaking) or a water bath.

Washing the Substrate Following the incubation, the substrate was taken out of the assembly solution and dip-washed in Milli-Q water. For the initial assembly step, that was done 3 times (i.e. the substrate was dipped into 3 centrifuge tubes with fresh Milli-Q water). For consecutive assembly steps, the substrate was washed 5 times.

A different (less harsh) washing method that will be referred to is *dilution washing*. For this washing, the centrifuge tube with the assembly solution and the substrate was completely filled with Milli-Q water. Afterwards, the solution was extracted by pipetting and only enough solution to cover the substrate was left in the tube. This procedure was repeated 5 times before extracting the substrate.

**Drying the Substrate** After washing the substrate, different methods of drying were used. For the initial assembly step with DNA functionalised particles, the substrate was blow-dried under a stream of nitrogen. For assembly steps that involved TMAC functionalised particles, the substrate was dried by placing it vertically on a paper wipe as can be seen in Figure 3.1d (unless otherwise specified). Typical drying times for the vertical drying in air were  $\sim 20$  min. In both cases, there was a water-air front moving from one side of the substrate to the other during the drying process.

# 3.5 Analyte Loading and SERS

As seen in the introduction chapter, plasmonic nanostructures can be used for surface enhanced Raman spectroscopy. This was also done with some of the here presented structures as will be described in Chapter 5. This section will address the experimental procedure for those measurements.

In order to get an idea of the plasmonic field enhancement of the different structures, the nanostructures had to be loaded with an analyte (benzenethiol, Figure 3.6). Prior to



Figure 3.6: Left: SEM image illustrating the effect of 20 min UV-Ozone treatment on nanoparticle assemblies. Right: Molecular structure of the analyte used for the SERS measurements.

loading, the charge carrying molecules needed to be removed as they would hinder analyte adsorption on the nanoparticles and also add noise to the Raman spectra. UV-Ozone treatment in combination with ethanol washing was chosen to remove those organics. During extended UV-Ozone treatment, the substrates would heat up and cause the nanoparticles to fuse together (Figure 3.6). The treatment was therefore done in 3 cycles of 4 min each with cool down periods in between. Following the UV-Ozone treatment, the substrates were dip-washed in EtOH (99%) to remove residual materials. The substrates were then dried under a  $N_2$  atmosphere. SEM imaging was used to confirm the intactness of the nanostructures.

Analyte loading was done by overnight incubation in a  $1 \mu M$  benzenethiol solution (in EtOH 99%) as per established protocol. [55,95] After incubation, the substrates were washed with ethanol again and dried in a N<sub>2</sub> atmosphere.

# Chapter 4

# Size Selective Adsorption of Gold Nanoparticles

This chapter focuses on the electrostatic dimer forming process and how different experimental parameters influence this process. Theoretical models will be used to understand the driving forces and develop a protocol for size selective nanoparticle adsorption onto preprepared substrates. The findings of this chapter are published in "Size Selective Adsorption of Gold Nanoparticles by Electrostatic Assembly". [174]



### 4.1 Electrostatic Dimer Assembly

As seen in the introductory section (page 23), the chosen assembly concept relies solely on electrostatic interactions to drive the formation of the nanoparticles on the substrate. For this purpose, a positive surface charge is confined on the SiO<sub>2</sub> substrate by functionalising it with APTES (Section 3.3.7). Similarly, charged molecules are confined on the AuNP surfaces (Sections 3.3.3 and 3.3.1). In the following section, the dimer forming process published by Zheng et al. will be reproduced and modelled using DLVO theory (Section 2.1.2). More details will be shown in Section 4.2.1 (page 66).

#### 4.1.1 Assembly Strategy

The prerequisites for the dimer assembly are the charged building blocks: A positively charged substrate and both negatively and positively charged particles. From here, the dimer assembly is a two step process (Figure 4.1): In a first step, the negatively charged (core) particles are adsorbed onto the substrate by immersing the substrate in the colloidal particle solution. In a second step, this substrate is immersed in a colloidal solution of positively charged (satellite) particles. The complex interplay between the electrostatic inter-particle and particle-surface forces creates a *funnelling* potential energy barrier that will be discussed in detail in the next section. This funnel guides the positively charged satellite particles towards the negatively charged cores. Once in contact, van der Waals interactions maintain the stability of the so produced dimers during the drying process.

#### 4.1.2 Theoretical Modelling

The interplay of the electrostatic and van der Walls forces will be looked at by using DLVO theory. This is done to find the parameters most critical to the assembly process. The first step of the assembly produces the adsorption centres for the subsequent step: As the positively charged substrate is immersed in the negatively charged particles, these particles get attracted by the substrate due to the opposite charges. The particles themselves repel each other, as they all carry a similar negative charge. Given that some thermal energy is provided during the assembly ( $65 \,^{\circ}$ C), this leads to a well separated distribution of the core particles on the substrate with a uniform nearest neighbour distribution. This distribution will be addressed in later experiments to elaborate the influence of the particle concentration in the assembly solution (Chapter 6).



Figure 4.1: Schematic illustration of the electrostatic, 2-step assembly process. Starting with a positively charged (green)  $SiO_2/Si$  substrate and negatively charged (red) particles (cores) an array of uniformly distributed cores is created in *step 1*. In a second step, these substrates are exposed to a colloidal solution of positively charged particles (satellites). The cores act as adsorption centres for these satellites, facilitating the dimer-forming process.

Looking at the second step, the total interaction energy  $E_{tot}$  for a positively charged satellite particle approaching a substrate with a core particle on it (Figure 4.2a) can be written as (see Section 2.1.2, page 29 for more details on the calculations):

$$E_{tot} = E_{rep} + E_{att} + E_{VdW} \tag{4.1}$$

The repulsive interaction energy  $(E_{rep})$  originates from the positively charged substrate and satellite particle whereas the attractive interaction energy  $(E_{att})$  is a result of the positively charged satellite interacting with the negatively charge core particle. The van der Waals contribution is also caused by the interaction of the satellite and core particles. The intensity of those interactions is strongly distance dependent, which can be seen in Figure 4.2b. The plot shows  $E_{tot}$  for a 60 nm particle vertically approaching a 30 nm particle on the substrate (for different ionic strengths of the assembly solution).

The approaching particle is exposed to a repulsive energy barrier. Only when this barrier is overcome, the particle reaches a location where the formed dimer is stable (i.e.  $E_{tot}$  is negative). Apart from changing the building blocks (e.g. particle size, charge), one can provide additional thermal energy by running the assembly process at an elevated



Figure 4.2: a) Schematic illustration of the setup of a positively charged satellite particle  $(2r_{+} = 60 \text{ nm})$  approaching the negatively charged core  $(2r_{-} = 30 \text{ nm})$  on the substrate. The approach path is indicated by the dashed vertical line. b) The total interaction energy  $(E_{tot})$  as calculated by DLVO theory for the setup in a) calculated for different ionic strengths of the assembly solution. The thermal energy of a satellite particle at 25 °C is indicated with the dotted line. c)  $E_{tot}$  as in b) for 25 µM NaCl solutions with different  $\zeta$ -potentials of the positively charged satellite particles.

temperature. The average thermal energy of a particle at 25 °C is indicated with a dotted line in Figure 4.2b. However, this allows only limited control as it also influences the mobility of the particles (as will be discussed in Section 4.2) and also gives rise to stability problems of the particle colloids at higher temperatures. Another, more applicable method is therefore the adjustment of the ionic strength of the liquid. This can be done by varying the NaCl concentration of the assembly solution. The introduced ions facilitate surface charge screening and thereby reduce the barrier height. This is also shown in Figure 4.2b for selected NaCl concentrations.

As the whole process is driven by the surface charges of the different components, changing these charges would also be an option to control the assembly. In Figure 4.2c, interaction energy calculations for satellite particles with a  $\zeta$ -potential of 50 mV (purple) and 70 mV (green) is shown. For the higher  $\zeta$ -potential, the barrier height increases as well. However, while a change of 20 mV of  $\zeta$ -potential is significant, its effect on the barrier hight is minor when compared to what can be achieved by varying the ionic strength of the solution.

In order to illustrate the *funnelling* mechanism and also present a more realistic scenario (as the particles do not always approach in a straight vertical line), the model had to be modified to allow lateral displacement of the satellite particle. When taking this lateral displacement l into account, an interaction energy map can be calculated with  $E_{tot}$  for a satellite particle at any given coordinate (l, z) with a core particle at (0, 0). Such a map for an assembly solution with a 25  $\mu$ M NaCl concentration is shown in Figure 4.3b. It is immediately visible that the satellite experiences a repulsive (red) funnelling potential that guides it towards the core particle where it can attach (blue).



Figure 4.3: a) A schematic similar to Figure 4.2 only with an additional degree of freedom: a lateral displacement l for the satellite particle is allowed. b) Total interaction energy map for an approaching positively charged 60 nm AuNP with a negatively charged 30 nm AuNP at (0,0). Red areas indicate repulsive interactions, blue areas attractive ones.

#### 4.1.3 Experimental Results

With the calculations presented in Section 4.1.2, it was possible to narrow down the assembly parameters to appropriate values to start with and thereby facilitate the experiments. However, the calculated parameters still needed optimisation to allow a maximum dimer yield as will be detailed in the following section.



Figure 4.4: Core particle assembly for 30 nm AuNPs. a) Overview SEM micrograph of a typical assembly (scale bar: 500 nm). b) High resolution SEM image of the same substrate (scale bar: 200 nm). c) Histogram of the nearest neighbour distance distribution of the presented substrate for a total of 294 particles. The average distance is 152 nm.

Dimer assembly was performed for two different satellite particle sizes (50 nm and 60 nm) with 30 nm core particles. After preparing the substrates and particle colloids, the cores were assembled by immersing the substrates in the core particle solution at 65 °C

for 2 h. A typical result can be seen in Figure 4.4. As expected, the particles assemble (mostly) separated from each other with a uniform nearest neighbour distance. This is due to the repulsive electrostatic interaction between individual core particles. Some particles assemble as dimers, which is likely a result of agglomeration already in the colloid during surface functionalisation and particle washing. The histogram in Figure 4.4c shows both, the uniform distribution around a mean nearest neighbour distance of 152 nm as well as the few dimer agglomerates (just above 30 nm).

The so-produced core assemblies were then used to fabricate the nanoparticle dimers by immersing the substrates in the satellite particle solutions. Different NaCl concentrations were trialled to reach the concentration with the highest dimer yield. As an example, the three fundamentally different situations are presented for the 30-60 dimer process (Figure 4.5a–d). The incubation time was in all cases 3 h. In the first case (a) the assembly was attempted with no NaCl in the solution, i.e. with the highest barrier for the process to happen. As expected the SEM images show a high amount of still unoccupied 30 nm core particles. After stepwise increase of the NaCl concentration, the point with the highest dimer yield was reached for a NaCl concentration of 25 µM (b and c). At this stage, the SEM images show only few unoccupied core particles. At the same time some satellite particles without a core particle can be observed. This non-specific adsorption on the substrate increases rapidly when increasing the NaCl concentration further (d). This observation is in good agreement with the theory: As the increased ionic strength of the assembly solution screens the surface charges, the satellite particles are not longer repelled strongly enough by the substrate to prevent attachment.

In general, the ionic strength was chosen as the main parameter to adjust the assembly behaviour throughout the project (and thus parameters such as  $\zeta$ -potential and temperature were kept constant). However, initially the  $\zeta$ -potential could not be controlled at the desired level, which allowed for the investigation of its effect on the assembly process. In Figure 4.5e and f the results for 30-50 dimer assemblies are shown. While keeping all other parameters constant, two different 50 nm particle batches were used: one with a  $\zeta$ -potential of 70 mV (e), the other one with 60 mV (f). The reduced  $\zeta$ -potential leads to a lower repulsive barrier for the dimer forming process (as seen in Figure 4.2c) and more non-specific adsorption of satellite particles can be observed in this case.



Figure 4.5: Different dimer assembly results for various assembly conditions: a) Assemblies with 60 nm satellites and no NaCl in the assembly solution (scale bar: 500 nm). b) Similar to a but with a 25  $\mu$ M NaCl concentration. Satellites that are not part of a dimer, are highlighted in red (scale bar: 500 nm). c) High resolution image of b) (scale bar: 200 nm). d) Similar assembly with a further increased NaCl concentration: 38  $\mu$ M (scale bar: 500 nm). d) Similar assembly with 50 nm satellite particles in a 25  $\mu$ M NaCl assembly solution (scale bar: 500 nm). e) A assembly with 50 nm satellite particles in a 25  $\mu$ M NaCl assembly solution (scale bar: 500 nm). f) Same as e) but with satellite particles with a reduced  $\zeta$ -potential (scale bar: 500 nm).

# 4.2 Size Selective Adsorption

The particle size is another parameter that strongly influences the potential barrier that the satellites have to overcome during their approach to the cores. This can readily be seen in Equations 2.2, 2.4, 2.5 and 2.6 in Chapter 2.1.2. This allows for the application of this technique to fields other than the previously presented plasmonic sensing [55]: The size-dependence of the electrostatic barrier can be used to hinder the adsorption of bigger nanoparticles while facilitating the adsorption of smaller ones, thus providing size-selective adsorption from a bidisperse satellite particle solution. Controlled adsorption techniques like this can be used to selectively deposit particle species from a mixed colloid onto a substrate. This selectivity could be exploited e.g. for targeted sensing and biomedical applications. [56, 59, 175–177] Different from already successfully demonstrated magnetic separation methods, [177–180] the proposed electrostatically driven process is independent of the nanoparticle material.

To investigate the size selectivity of the electrostatic dimer-forming process, interaction

energy maps and activation energy barriers for different satellite particle sizes will be calculated and then compared to an experimental study of the adsorption of satellite particles from bidisperse solutions.

#### 4.2.1 The Theory

#### **Potential Landscape and Barrier**

Similar to the previous section, the interaction energy maps are used to visualise the different potential funnels for the two differently sized satellite particles. The calculations are based on the parameters as used in the experiments later on (Section 4.2.2). The resulting maps can be seen in Figure 4.6a (left: 50 nm, right: 20 nm). Both cases show the gradient in the (repulsive) interaction energy guiding the approaching particle towards the adsorption site (the core particle). It is also evident that there is a barrier present that particles have to overcome in order to reach the core particle. This is more evident in Figure 4.6b for an approach path perpendicular to the substrate (at l = 0). At 20 °C the barrier for a 20 nm particle is 50 meV. This is only  $0.5k_BT$  (12 meV) higher than its mean thermal (kinetic) energy (Figure 4.6b, green line). For the 50 nm AuNPs, the barrier is in turn  $4.8k_BT$  (120 meV) higher than its mean thermal energy (Figure 4.6b, blue line). While for the 20 nm particles the barrier height is in a range where experiments (in Figures 4.2 and 4.5 and in literature) have shown high yield electrostatic dimer assembly, for the 50 nm ones the barrier is in a range where dimer formation is not efficient. [55]

#### Accounting for the Maxwell-Boltzmann Distribution

To roughly estimate the effect of this difference in barrier heights on the nanoparticle assembly process, the Maxwell-Boltzmann kinetic energy distribution of the particles at 20 °C were calculated (Figure 4.6c). For more details on the Maxwell-Boltzmann distribution see Section 2.2 (page 33)

In Figure 4.6c  $A_{20}$  ( $A_{20} = 0.266$ ) and  $A_{50}$  ( $A_{50} = 0.007$ ) represent the fraction of the population of the 20 or 50 nm particles (respectively) that has a thermal energy higher than the corresponding barrier. Using this very simple approach, the adsorption of the 20 nm AuNPs is favoured (by a factor of 38:1) as there is a higher fraction of 20 nm AuNPs with an energy higher than their adsorption barrier. With these calculated population fractions, the concentrations of the differently sized particles in the area where the repulsive interaction reaches its maximum (the location of the barrier) can now be compared. The particles



Figure 4.6: Interaction energy landscapes: a) Calculated maps of  $E_{tot}$  of a positively charged AuNP (left: 50 nm, right: 20 nm) at position (l, z) and a negative 30 nm AuNP (indicated in yellow) sitting on a positively charged surface at (0, 0). Blue colours indicate attractive and red indicate repulsive interaction energies. The dotted lines mark where the  $E_{tot}$  equals the mean thermal energy of the particles (at 20 °C). b) Dependence of  $E_{tot}$ for differently sized particles on z when approaching vertically towards the core particle (l = 0). The black dashed line indicates the mean thermal energy at 20 °C. c) Maxwell-Boltzmann distribution (orange) at T = 20 °C. The black dashed line indicates the mean thermal energy of the particles, the blue and the green line mark the energies of the barriers for 50 and 20 nm particles (as shown in b).

are exposed to a repulsive potential corresponding to their size. Therefore, only particles with an energy equal or higher than this potential are expected to be located in this area. Particles with lower energy are driven away to areas with lower  $E_{tot}$ . That suggests a 38 times higher concentration of 20 nm particles at this point (assuming equal numbers of 20 nm and 50 nm particles in the initial solution). This, in turn, would lead to a higher probability for 20 nm satellite particles to adsorb on the cores and thus a size-discriminative adsorption process.

#### Influence of the Particle Zeta-Potential

The theoretical effect of the core and satellite particle  $\zeta$ -potentials on the size-dependence of the barrier was investigated as well. From these calculations (see Figure 4.7) it can be seen that in order to increase the barrier height differences for 20 and 50 nm particles, a higher  $\zeta$ -potential for the satellite particles is beneficial and thus a maximization of these potentials was pursued experimentally. Calculations show a similar effect for a reduced core-  $\zeta$ -potential, however, this would have an adverse effect on the overall dimer yield, as there would be less guidance towards the cores.



Figure 4.7: Satellite particles size dependence of the calculated adsorption barrier height. a) The size dependence for 3 different satellite particle  $\zeta$ -potentials (while keeping the core  $\zeta$ -potential constant).  $E_1$  an  $E_2$  represent the difference in barrier height of a 20 and 50 nm particle for the lowest (orange) and highest (blue)  $\zeta$ -potential, respectively. b) Similar to a), however, this time the core particle  $\zeta$ -potential is varied for a fixed satellite particle charge.

#### **Diffusion Effects**

Besides these surface charge induced selectivity effects, we can further use the Stokes-Einstein-Sutherland (SES) equation to estimate how the particle size affects their diffusion and whether that leads to an enhanced selectivity:

$$D = \frac{k_B T}{6\pi\eta r},\tag{4.2}$$

With  $\eta$  as dynamic viscosity and r the radius of a spherical particle. Due to this inverse proportionality to the particle radius, the 20 nm particles are expected to diffuse 2.5 times faster than the 50 nm ones. This higher diffusion speed is another factor that contributes to the preferential adsorption of the 20 nm particles (assuming a kinetically driven process).

#### 4.2.2 Experiments

In order to investigate the just described system, silica-coated silicon  $(SiO_2/Si)$  substrates and colloidal AuNPs were functionalised with charge carrying molecules (as per protocols described in Chapter 3). Negatively charged 30 nm AuNPs were then assembled onto the positively charged substrates to provide adsorption centres for the positive particles. Positively charged 20 and 50 nm AuNPs were mixed to form a bidisperse colloid (satellite particle solution). For the size-selective adsorption step, dried substrates with the core assembly were immersed in the satellite particle solution for a fixed amount of time at a constant temperature. Assembly performance was assessed using SEM imaging and UV-vis spectroscopy.

As a measure of the effectiveness of the size-selective assembly process, we have defined a selectivity factor (SF):

$$SF = \frac{(N_{20} : N_{50})_{captured}}{(N_{20} : N_{50})_{solution}},$$
(4.3)

Where N is the number of particles, either captured on the substrate or initially present in solution. The selectivity factor is a measure of how much the 20 to 50 nm particle ratio has increased on the substrate when compared to the solution. A SF = 1 means that the substrate is not selective, SF < 1 indicates preferential adsorption of the 50 nm particles. SF values greater than one indicate a selectivity towards the 20 nm particles (e.g. SF = 2 means that the 20 to 50 nm particle ratio doubles on the surface compared to in solution). Based on the electrostatic analysis shown above one would expect an ideal selectivity factor of up to 38 (not taking diffusion into account) and a maximum of 95 when using the simple diffusion model as well.

In the next section, particle statistics and exemplary SEM images show the adsorption statistics and patterns for different assembly conditions. Adsorption statistics were derived from SEM images. The effect of the solution temperature, the incubation time and the mixing ratio on the size-selectivity of the electrostatic self-assembly were investigated.

#### The Influence of the Temperature

In order to vary the mean energy of the particles (dashed black line in Figure 4.6) and the particle diffusion speed, the temperature at which the adsorption process took place was varied. This consequently changed the difference between the  $E_{tot}$  of the barrier and the mean thermal energy of the particles  $(1.5k_BT)$ , and the speed of the process (as particle diffusion is slowed down at lower temperatures).

Comparing the adsorption behaviour of incubations at 21 °C and 14 °C after 5 h, while keeping all other parameters fixed leads to two observations (Figure 4.8): Firstly, the overall coverage of the adsorption sites is much higher at 21 °C compared to the lower temperature. This is to be expected, as the thermal energy of the particles is lower in the second case, which slows the process down (as at this temperature a lower fraction of the particles has a thermal energy higher than the barrier). The much lower yield also indicates that the particle diffusion towards the surface slows down, which is in accordance with the SES equation for the diffusion constant (see Equation 4.2). Secondly, the selectivity factor for the lower temperature is SF = 9.8, more than twice as high as for the 21 °C incubation and represents an almost ten-fold increase of the 20 to 50 nm particle ratio when compared to solution. A higher selectivity at lower temperatures is expected, as the Maxwell-Boltzmann distribution is temperature dependent. That leads to a higher theoretical selectivity factor as the fractions of population (Figure 4.6c,  $A_{20}$  and  $A_{50}$ ) change for the differently sized particles by a different amount. This effect can be seen in Figure 4.8e where the ratio  $A_{20}/A_{50}$  is plotted for different temperatures. The slower process dynamics mentioned above also contribute to the higher selectivity at lower temperatures as will be shown in the next section.

#### The Effect of Incubation Time

The adsorption mechanism is a process where particles must overcome an energy barrier higher than their mean thermal energy. Therefore, it is of interest to investigate the time dependence of the process and compare the influence of the incubation time in step 2 of Figure 4.1 on the fractions of adsorbed 20 and 50 nm satellite particles. This is especially interesting as the process seems to be more selective but slower at lower temperatures.



Figure 4.8: Effect of temperature and incubation time on the assemblies when having equal amounts of 20 and 50 nm particles in solution. (a) Top: A comparison between the percentage of 50 nm particles in the initial assembly solution (orange) and adsorbed on the surface (blue) for different assembly temperatures and incubation times. Bottom: The overall adsorption yield (i.e. core particles with a satellite attached) for the different assembly conditions. (b-d) SEM images showing representative results for the 3 different assembly conditions (20 and 50 nm particles indicate in green and blue, respectively): b) Incubation at 21 °C for 5 h. c) Incubation at 14 °C for 5 h. d) Incubation at 14 °C for 22 h (scale bars: 250 nm). e) A plot of the calculated  $A_{20}/A_{50}$  population ratio as function of temperature as introduced in Figure 4.6c.

Therefore, 5 h and 22 h incubation times (at 14 °C, see Figure 4.8 c and d) were compared and it was found that the longer time leads to a full coverage of the adsorption sites. At the same time, the amount of adsorbed 50 nm particles increased by 8% with increased time. This reduction of the selectivity might seem contradictory to the theoretical model at first. However, a closer look at the SEM images (Figure 4.8d) reveals a high yield of multimers (i.e. core particles with more than one satellite particles attached) as opposed to mainly dimers found for the shorter incubation time. That means that the dimer forming model, its barrier heights and the calculated selectivity factor are not fully applicable anymore for this situation. An interaction energy map (similar to the one presented in Figure 4.6) for a 20 nm particle approaching an already formed core-20 nm dimer shows that the barrier has now greatly increased to  $7.3 k_B T$  (184 meV). For this barrier, the Maxwell-Boltzmann distribution yields a fraction of population of particles with higher energy of only 0.2%. Furthermore, the model does not account for attractive or repulsive effects resulting from additional core particles in the close proximity of the investigated core. Due to the given reasons, the considerations based on the dimer forming model reflect the experimental situation best at a low dimer coverage and size-selectivity is reduced after higher dimer coverage is reached.

An additional experiment was undertaken to address the question whether the adsorption process is thermodynamically or kinetically driven. In a thermodynamic equilibrium state, already adsorbed particles would also desorb again and thereby render a core particle available for a new adsorption to take place. In a kinetically driven process, satellite particles would not desorb again once captured by a core particle. Two samples were run though the adsorption process with an incubation time of 5 h. After the incubation, one sample (*sample A*) was washed as per the protocol we have described above. The second sample (*sample B*) was immersed in 600 ml of Milli-Q water, being in solution at all times (see Figure 4.9).

For the case of a reversible process (thermodynamically driven) one would expect less satellite particles to be adsorbed on the cores of *sample B*, due to reversible adsorptiondesorption events. Additionally, one would expect a significant difference in the 20 nm to 50 nm satellite ratio on the surface if a desorption process was size dependent (e.g. due to different van der Waals interaction energies for 20 nm and 50 nm particles). However, the 20 nm to 50 nm particle ratio did not differ significantly for both samples (*sample A*: 6.1, *sample B*: 7.7, standard deviation: 1.5). The same is true for the overall yield of adsorbed



Figure 4.9: Schematic workflow of the experiment to determine the desorption behaviour of adsorbed satellite particles. The sample A represents as reference sample, for sample B desorption was attempted. The statistics of the final results for both samples are shown in the plot.

particles (65% and 68% with a standard deviation of 10%; sample size > 1000 counts for each substrate; Figure 4.9). It can therefore be concluded that no significant desorption of satellite particles occurs after adsorption to a core, which indicates a diffusion controlled process, rather than a fully thermodynamically controlled one. This also explains why the considerations presented in Figure 4.6 are more accurate for shorter incubation times where many unoccupied core particles are available for adsorption of satellite particles.

#### Changing the particle mixing ratio

The dependence of the selectivity on the initial mixing ratios of the two differently sized satellite species in the bidisperse colloid was investigated as well. The results shown here were achieved with an incubation time of 3 h at 20 °C. A summary of the results is shown in



Figure 4.10: Effects of the mixing ratio in solution on the selectivity of the adsorption process. Top: SEM-based adsorption statistics showing the amount of adsorbed 50 nm particles on the surface (blue) when using different 20 to 50 nm particle mixing ratios in the initial assembly solution (orange: percentage of 50 nm particles in solution). The batch numbers are a reference for the different mixing ratios (*batch 1*: 19:1, *batch 2*: 2:1, *batch 3*: 1:1, *batch 4*: 1:2). Bottom: The selectivity factor for different mixing ratios calculated from the adsorption statistics according to Equation 4.3.

Figure 4.10, where the initial mixing ratios between 20 and 50 nm AuNPs of the different batches (no. 1 - no. 4) were 19:1, 2:1, 1:1, and 1:2 (respectively).

Due to the superior number of 20 nm particles in *batch 1*, it is not surprising to have mainly 20 nm particles adsorbing on the core particles. The number of the small satellites adsorbed on the surface did indeed increase from 95% to 98% as can be seen in Figure 4.10, batch 1, blue bar (indicating a 3-fold increase of the 20 nm particle concentration at the surface). When increasing the fraction of the 50 nm particles in the bidisperse colloid further, the selectivity factor increased as well significantly to a maximum value of 28, which is reached with equal particle ratios in solution (batch 3). This result shows that the electrostatic self-assembly method is suitable to increase the fraction of the 20 nm AuNPs to over 96% when starting with a 1:1 mix of 20 and 50 nm AuNPs. An SEM image of the resulting adsorption pattern is depicted in Appendix B.1. Increasing the 50 nm particle fraction further to 67% leads to an increased fraction of adsorbed 50 nm particles of 23% indicating that the selectivity of the adsorption process decreases significantly when increasing the 50 nm content further.

#### UV-Vis Spectroscopy to Track the Selective Adsorption

The mixing ratio of *batch 1* (95% 20 nm AuNPs) is approximately equal to an optical density ratio of 1:1. Therefore it was used (at a highly diluted absolute particle concentration) as evidence for the preferential adsorption by comparing the UV-Vis spectra before and after the adsorption (Figure 4.11). The AuNP colloids show a pronounced plasmon resonance peak in the UV-Vis absorbance spectrum, which is at a different wavelength for 20 and 50 nm AuNPs. [181,182] The measured spectra for a bidisperse colloid are therefore a sum of those two spectra. Depending on the mixing ratio, the peak position of this sum is closer to the absorption peak of the particle species with the higher optical density (~ particle concentration) in the mix. The UV-Vis spectra in Figure 4.11 show that the peak position of the assembly solution is red-shifted (which is closer to the resonance peak of a 50 nm AuNP colloid) after a successful selective adsorption experiment. The peak position was hereby compared to a control sample of the same solution that underwent the same process *without* a substrate in it (i.e., without selective adsorption). These measurements indicate that the 20 nm AuNP concentration in the mixed solution did drop during the experiment, which further supports the statistical analysis of the SEM images.

#### **Concluding Remarks**

The observed variations of the selectivity factor show strong dependence of the size-selective adsorption process on the assembly conditions. While the process shows the predicted preference for the adsorption of smaller particles (which could not have been explained based on a simple diffusion model), the observed variations of the selectivity factor cannot



Figure 4.11: Absorption spectra of the 20-50 nm particle solution for an adsorption experiment as in *batch 1*. The green line was taken from the solution after the adsorption process, the orange was from a control solution which was run through the same process only without an adsorption substrate. Dashed lines indicate the fits to determine the peak position.

be described by the considerations summarised in Figure 4.6 alone. As discussed earlier, the electrostatic interaction model describes the formation of a dimer, neglecting multiparticle effects (e.g. neighbouring core particles, multimer formation or satellite particle interactions in the solution). A possible approach to further enhance the selectivity of the size-selective adsorption process at higher initial mixing ratios is to increase the  $\zeta$ -potential on the TMAC-AuNPS (Figure 4.7) which may require the use of different surface-capping ligands. This increase is expected to increase the difference in the adsorption barriers of the differently sized particles (see  $E_1$  and  $E_2$ ) and therefore also for the adsorption yields for the different species.

# 4.3 Summary

In this chapter the fundamental concept of the electrostatic nanoparticle assembly which had been introduced by Zheng et al. was studied in detail. Theoretical DLVO calculations were used to get a detailed understanding of the influence of parameters such as ionic strength and particle  $\zeta$ -potential on the dimer-forming process. Calculated maps of the interaction energy of this process helped to visualize the funnelling potential responsible for the dimer formation and to narrow down the parameter range for the experiment. The expected effects of the parameters were then confirmed in experiment and asymmetric nanoparticle dimers could be produced with different satellite particle sizes.

Subsequent sections focused on the satellite particle and its effect on the dimer forming process, as this presented a new concept for size-selective nanoparticle sorting. Using the same theoretical framework as before, calculations indicated that not only the potential barrier height, but also incubation time, temperature and relative particle density (i.e. satellite particle mixing ratio) are crucial parameters. This is a result of introducing the Maxwell-Boltzmann distribution for the particle energies leading to the barrier being not longer treated as a sharp limit below which no dimer-formation is possible at all. The different parameters were then experimentally investigated and optimised for a bidisperse satellite particle solution with 20 and 50 nm AuNPs. A maximum selectivity factor of SF = 28 could be reached for an initial 1:1 mixing ratio. An additional result of this chapter was the assembly of a smaller satellite particle on a bigger core particle for the first time with this technique. This ability is a crucial prerequisite to move on to the more complex hierarchical trimer assembly in the next chapter.

# Chapter 5

# **Plasmonic Trimer Nanolenses**

The focus of this chapter will be on the fabrication of nanoparticle trimer systems by advancing the electrostatic assembly concept further. In particular, self-similar plasmonic nanolenses will be assembled and investigated in detail to explain their plasmonic properties. This contributes to the ongoing discussion about theoretical studies of such systems and sheds light on the electric field focusing capabilities of these trimers. The findings of this chapter are published in "Plasmonic Nanolenses: Electrostatic Self-Assembly of Hierarchical Nanoparticle Trimers and Their Response to Optical and Electron Beam Stimuli". [183]



# 5.1 The Concept

After detailed investigation of the electrostatically driven assembly of AuNP dimer systems, the next logical step towards more complex structures was the addition of a third particle, and thus the assembly of nanoparticle trimers. The ultimate goal here was to develop a high yield assembly process for trimeric plasmonic nanolenses such as (but not limited to) the ones suggested by Li et al. [38] An example of such a trimer can be seen in Figure 5.1.



Figure 5.1: Schematic (top inset): Geometry of the gold nanoparticle trimers investigated in this study with different particle radii ( $r_1 = 10 \text{ nm}$ ,  $r_2 = 15 \text{ nm}$ ,  $r_3 = 25 \text{ nm}$ ), centre-centre distances ( $s_1$ ,  $s_2$ ) and interparticle gaps ( $d_1$ ,  $d_2$ ). 3D-plot: Electrical field enhancement plot calculated by a fully retarded boundary element method (Section 2.3.2) for a trimer upon incident plane-wave illumination at 610 nm perpendicular to the x-yplane (without substrate). The field is calculated for a plane containing the centres of all the particles. Particle cross sections are indicated in yellow.

#### 5.1.1 Motivation and Background

While nanoparticle dimers are well explored and utilised as plasmonic lenses, experimental studies on hierarchical nanoparticle trimers are (although theoretically extensively studied) quite limited. This is surprising, as Li et al. (and others after them) predicted that much greater field localization could be achieved with self-similar arrangements of at least three nanoparticles. They report plasmon modes with a very strong field localization in the gap between the two smallest particles (as discussed in Chapter 1.2.3; see Figure 5.1). This plasmonic lensing effect cannot be achieved to that extent with chains of equally sized particles. In the next section, the electrostatic assembly concept will therefore be extended to produce such structures. Subsequently, the ability of the self-assembled trimers to focus light is ascertained experimentally via optical, cathodoluminescence and electron

energy loss spectroscopy, and theoretically via an analysis of the optical properties of the nanoparticle trimers in terms of surface plasmon eigenmodes. This will contribute to the ongoing discussion about those nanolenses and also provide a simple and scalable way to produce them.

#### 5.1.2 The Assembly Concept

It was shown by Zheng et al. that for a 30 nm particle, the likelihood of two satellite particles to attach to the same core particle was low. [55] Therefore the hypothesis of this project was that the attachment of two satellite particles could be achieved by using a three step assembly process. The substrate drying in between each step would cause the satellite particles to come to sit next to the core, rather than on top of it, thereby enabling the adsorption of a second satellite in the next step.



Figure 5.2: The simple idea of turning an assembled dimer into a trimer by adding the 3rd particle in a second satellite assembly step.

### 5.2 Feasibility Tests

#### 5.2.1 50-30-60 nm Trimer Structures

To experimentally test the feasibility of this concept, attaching a 60 nm AuNP to a 30-50 nm dimer was attempted (as parameters for 30-50 nm and 30-60 nm dimers were well developed). This would yield trimer structures similar to the ones suggested by Toroghi et al., where a smaller particle is positioned between two bigger ones. [184,185] The results of these experiments can be seen in Figure 5.3a and b. Similar to the dimer forming step, the ionic strength of the assembly solution was used to adjust the assembly results: A too low NaCl concentration would not allow a high trimer yield while a too high one would cause nonspecific adsorption of the satellite particles on the substrate (Figure 5.3b, orange). The best trimer yield of 33% was achieved for a 40 µM NaCl concentration at 25 °C. With these encouraging results, the proof of concept was a success and the trimer assemblies with 20 nm AuNPs could be approached, as will be detailed below.



Figure 5.3: Different nanoparticle trimer assemblies (scale bars: 500 nm): a) SEM image of a three step assembly of 50-30-60 nm trimers (trimers highlighted in green). Some non-specifically adsorbed 60 nm AuNPs are visible (orange). b) Similar to a) but with an increased ionic strength of the assembly solution in the last assembly step. c) Assembly results for attaching 20 nm AuNPs to 30-50 nm dimers at 30 °C. A lot of non-specifically adsorbed 20 nm are visible on the substrate.

#### 5.2.2 Expanding 30-50 nm Dimers to Nanolens Trimers

After the success with the 50-30-60 nm trimers, the initial idea for the nanolens assembly was similar: The established 30-50 nm dimers would be used and the 20 nm AuNPs added in the last step. However, due to the lower potential barrier for the adsorption of 20 nm AuNPs compared to 50 nm ones (as has been shown in Chapter 4), the optimisation was non trivial. The increase in the ionic strength of the assembly solution could not be achieved without the formation of multimers and nonspecific adsorption of 20 nm particles. Therefore, the temperature of the assembly solution was altered in order to change the thermal energy of the particles. This led to a significant trimer yield, however, the nonspecific adsorption of 20 nm could not be prevented, as can be seen in Figure 5.3c for a 30 °C assembly.

# 5.3 Developing the Final Assembly Protocol

Due to the issues experienced, a new assembly strategy was proposed. A possible reason for the low trimer yield at lower temperatures can be rationalised using the total interaction energy map of the system. In the case where the 20 nm AuNP is added as a last particle, there is already a 50 nm particle with a repulsive charge sitting next to the 30 nm AuNP (the adsorption point). It is therefore beneficial to add the 50 nm AuNP last, as the 20 nm AuNP next to the 30 nm AuNP would present a less repulsive barrier. Similar to the trimer assemblies before, one would expect the second satellite particle to be located opposite the first one. This can be seen from the DLVO calculations in Figure 5.4 where the yellow



Figure 5.4: The total interaction energy map for a 50 nm particle approaching a 20-30 nm dimer on the surface. The yellow dashed line indicates the approach path with the lowest energy barrier.

dashed line indicates the approach path with the lowest potential barrier.

These considerations led to the final assembly concept that is presented in Figure 5.5. The interaction energy maps for both satellite adsorption steps can be seen in Figure 5.5a and b. In both cases a clear funnel is visible, the 20 nm AuNP seems to only slightly distort the funnel for the 50 nm adsorption.

In order to accomplish the new strategy (Figure 5.5c), it is necessary to achieve high yield 20 30 nm dimer assemblies. This had proven challenging in the past, as the selflimiting effect of the dimer-forming step is reduced for smaller satellite particles. [55] The controlled dimer fabrication had not been demonstrated for this configuration. Figure 5.5d–f show SEM images of the desired assembly outcome of each step of the new assembly strategy. The optimisation process to achieve those results is outlined in the next paragraphs.

By using DLVO theory, the different situations can easily be visualised in Figure 5.6 where the potential maps for a 20 nm satellite and a 50 nm satellite approach are calculated. For the 50 nm particles the electrostatic funnel is narrower, thereby efficiently preventing the adsorption of a second satellite in the same assembly step: Once one satellite adsorbs on the core, it blocks the approach path for any other particle. A trimer assembly can here only be attempted after the drying step in which the satellite particle moves from an "on top" position to an "on the side" position.

For the 20 nm approach however, the shape of the repulsive funnel does allow for a more "on the side" position of the satellite particle during the assembly (without drying). A high yield of multimers (one core with several satellites attached) is expected when using the same assembly conditions when compared to the bigger particles. A typical assembly



Figure 5.5: Overview of the final electrostatic assembly process: a) Total interaction energy map for a 20 nm AuNP approaching a 30 nm core particle on the substrate in step 2. Repulsive forces are indicated in red, attractive in blue. The dashed lines indicate where  $E_{tot} = 1.5k_BT$ . b) Similar map as in a) for step 3 with a 20 and a 30 nm particle already on the substrate and a 50 nm satellite approaching. c) Schematic of the proposed assembly process from negatively charged core particles on a positively charged substrate in step 1 to trimers by subsequently adding positively charged particles of different sizes in steps 2 and 3. Surface confined charges are indicated in green (positive) and red (negative). d)-f) High resolution SEM micrographs showing the results of each assembly step (scale bar: 250 nm).


pattern for these conditions can be seen in Figure 5.7a. Only few dimers are formed

Figure 5.6: Comparison between the total interaction energy maps for a 20 nm (left) and 50 nm (right) satellite approaching a negatively charged 30 nm core particle on the substrate (as calculated by DLVO theory).

during that procedure, most structures feature a minimum of three 20 nm satellites. From the previous experiments, different options to mitigate this problems where considered. Finally, it was found that adjusting the particle concentration in the assembly solution together with the incubation time produced the best results. In principle, a reduction of the assembly temperature would also have been an option. Changing only the incubation time would have been possible as well, however, the necessary drastic reduction would have caused a high sensitivity to small changes in the assembly time (which can easily occur during experiment). This would adversely affect the reproducibility. The results shown in Figure 5.7b were achieved with an incubation time of 2.5 h at 25 °C with a particle solution optical density of 1. No NaCl was added to lower the adsorption barrier.



Figure 5.7: SEM micrographs of the 20-30 nm dimer forming step. a) When using the standard satellite particle assembly conditions, as used for dimer assembly with sizes between 30 and 60 nm, mainly multimers are observed. b) Assembled 20-30 nm dimers assembled with optimised conditions. (scale bars: 250 nm)

After successful assembly of the 20-30 nm dimer, the final trimer assemblies can be achieved by adding the 50 nm particles in the third assembly step. The same assembly parameters as for the usual 30-50 nm dimer assembly are used and the ionic strength was optimised to achieve high trimer yield with minimal unspecific adsorption of 50 nm particles on the substrate. This process has been explained in detail before in Chapter 4.1.3 (page 63) and is therefore not explained here. A NaCl concentration of 25  $\mu$ M was found to produce the best results.

# 5.4 Structural Analysis

In Figure 5.8a, a larger scale SEM micrograph of the final assembly with trimers highlighted in green shows the distribution and variety of the assemblies (an additional SEM image can be found in Appendix C.1). The results of a statistical analysis of the assemblies (of 621 individual assemblies) are presented in the inset. 63% of all observed structures are trimer structures, of these, 59% are rather linear, as expected from the DLVO calculations (Figure 5.4). The classification into rather linear, bent or collapsed trimers is done as shown in Figure 5.8c: Trimers assembled completely straight and up to a bending angle of  $\alpha = 55^{\circ}$  are regarded as ideal, as calculations did not show significant changes in the plasmonic properties (as will be shown later, Figure 5.12). Assemblies with a bending angle greater 55° up to where a gap between the 50 and 20 nm particle is still well recognizable are counted as bent trimers. Collapsed trimers feature a 20 nm particle similarly close to the 30 and 50 nm particle.



Figure 5.8: a) SEM overview image of particle assemblies on a SiO<sub>2</sub>-coated Si substrate with trimeric structures coloured in green (scale bar: 500 nm). b) Statistical evaluation of the assemblies based on SEM data comprising 621 individual assemblies (assembly patterns indicated in white, 6% unassigned). c) Pictograms indicating how the classification of the different trimer and tetramer structures was done. Depicted are (clockwise from top left) the linear trimers with a maximum angle  $\alpha = 55^{\circ}$ , the bent trimers and the collapsed ones. Any 30-50 nm dimer with two 20 nm particles was considered a tetramer.

20% of the structures are dimers (20-30 nm) which did not form trimers in the third step. However, further lowering of the adsorption barrier to facilitate a higher yield by increasing the ionic strength would lead to increased nonspecific adsorption of 50 nm satellites on the substrate (as shown for dimers in Figure 4.5d, page 65). One can also see the limitations of the dimer forming step (step 2), as 12% of the 30 nm cores have two 20 nm satellites attached. A less pronounced self-limiting effect (i.e. exactly one satellite attaching to the core) for the dimer forming step for smaller satellites compared to bigger satellites has been observed before (Section 5.3). [55,174] Such assemblies with two 20 nm satellites result in tetramers when adding the 50 nm satellite in the last step.

# 5.5 Characterisation

With the method described above, one of the two main goals of this chapter has been achieved: The high yield fabrication of hierarchical AuNP nanoparticle trimers. The so fabricated trimers can now be investigated to determine their plasmonic properties and lensing behaviour.

# 5.5.1 Optical Analysis

In a first step, optical absorbance spectra are measured by UV-vis spectroscopy of the assemblies on glass substrates. In doing so, an average spectrum of multiple structures is acquired, as the beam of light measures an area of  $\sim 1 \text{ mm}^2$ . This will have to be taken into account when analysing the results. At the same time, this resulted in statistical representative results for a large area.

The optical absorbance spectra for the core, dimer and trimer assemblies are shown in Figure 5.9a. Starting from the core particles, the spectrum exhibits a single absorption band, characteristic of a localized surface plasmon resonance of individual particles (Figure 5.9b, orange). Within the electrostatic limit, applicable in this instance due to the small particle size ( $\lambda$ /size  $\gg$  1), the position in wavelength of this plasmon band is expected to occur at ~ 526 nm according to the Fröhlich resonance condition (Equation 1.2). As noted before, the inhomogeneous refractive index surrounding the core particles (due to the presence of the substrate) results in a redshift of the spectrum.

When the dimers are formed, an additional resonance at around 580 nm arises, as evidenced by the shoulder in the spectrum shown in Figure 5.9b (blue). This resonance occurs at a wavelength that is different from that of the localized plasmon resonance of individual core or satellite particles (see Sections 3.3.1 and 3.3.3). The new absorption band occurs due to the near-field coupling of the particles, which leads to a longitudinal



Figure 5.9: a) UV-vis absorption spectra for core (orange), dimer (blue) and trimer (green) assemblies on a glass substrate. b) Retarded boundary element method calculations for absorption spectra for dimer and trimer (combining different arrangements according to their statistical occurrence) assemblies. Dashed lines indicate the spectra for a single linear trimer excited along the longitudinal (dark grey) or transversal (light grey) direction. c) Schematic of a 20-30-50 nm trimer on a substrate. The dotted line shows the alignment of the particle centres.  $E_0$  is the E-field of the incident light which has a transversal ( $E_{trans}$ ) and a longitudinal ( $E_{long}$ ) component with respect to the axis of the trimer on the substrate. d) Calculated absorbance spectra for the most commonly found assembly structures. Adding those spectra according to their statistical occurrence yields the trimer spectrum shown in b.

coupled-resonance of the dimer. [55, 186, 187]

Figure 5.9b shows the spectrum of the final trimer assembly, which exhibits a further red-shifted shoulder at  $\sim 610$  nm. This new absorption band occurs due to the inter-particle interactions of the three particles in the trimer assemblies. They result in a localized plasmon resonance which will now be discussed in detail.

Interaction of light with the self-assembled structures will be described using (retarded) BEM calculations (as explained in Section 2.3). The starting point in these numerical simulations is the geometry of the trimer (or dimer) and the dielectric properties of the trimer and its surroundings. TEM measurements were used to confirm the sizes of the nanoparticles. Perfect spherical particles with diameters of 20, 30 and 50 nm are assumed for the calculations, the distribution of particle sizes and shapes in the experiment was thereby neglected. Different particle centre heights on a substrate were taken into account by combining transversal and longitudinal signal as shown in Figure 5.9c.

Dimer assemblies were used to estimate the average inter-particle gaps for 20-30 nm dimers ( $d_1 = 1.1 \text{ nm}$ ) and for 30-50 nm dimers ( $d_2 = 1.7 \text{ nm}$ ) via a pseudo fitting procedure described by Zheng et al. (Figure 5.10). [55,187,188] Further discussion on the inter-particle gap size can be found at the end of this chapter. For the dielectric constants of gold, the



Figure 5.10: The wavelength position of the calculated longitudinal resonance peak of a 20-30 nm dimer in dependence of the interparticle gap size (blue markers). The actual gap size is estimated by using a resonance peak closely matching the experimental results (black arrows).

tabulated values by Johnson and Christy were interpolated. [17] The refractive index of the surrounding medium was fixed to 1.3, as it was found that this value closely represents the dielectric environment of metal particles located at an air/glass interface. [55,189,190]

The analysis of SEM images revealed that not only linear, but also angled trimers are present (as shown in Figure 5.8). The adsorption spectra for the four major geometric arrangements present (accounting for 80% of all found structures, see Figure 5.8b) were simulated: the three differently aligned trimer species and a 20-30 nm dimer. The calculated spectra of these structures were then combined to produce the final spectrum using their statistical occurrence as weight. The individual spectra can be seen in Figure 5.9d. The results agree well with experimental data in terms of relative peak heights and positions. A slightly blue-shifted higher energy peak is observed for the calculations, which is expected as the substrate was not explicitly included in the calculations. The measured spectra also have less pronounced peaks than the calculated ones, which can be attributed to the finite particle and gap size distribution of the AuNP colloids.

When separating the spectrum of a linear trimer into a transversal and a longitudinal plasmon resonance, one can see that the observed lower energy resonance is purely longitudinal (Figure 5.9b). At this wavelength, the surface charge distribution of the free electrons is predicted (using a retarded BEM calculation) to exhibit a strong localization in the region of space between the two smaller particles (see Figure 5.11a). This leads to a strong localization of electric field in what has previously been called a plasmon lensing effect. [38] The lensing effect is evident on a calculated map of the electric fields around the trimers (for a 614 nm excitation wavelength) as shown in Figure 5.11a, which shows a strong  $|E/E_0|^2 \sim 10^5$  localization of the electric field in the gap between the two smallest particles.

#### 5.5.2 Plasmon Eigenmode Expansion

In order to get a more physical description of the inter-particle interactions responsible for this effect, the trimer will now be described in terms of superpositions of eigenmodes, an approach that is strictly applicable only to assemblies with sub-wavelength dimensions (Section 2.3.1, page 38). In general, the plasmon resonance peak positions derived from EEM can differ slightly from those obtained by the retarded BEM calculations, however, this method offers the opportunity to provide a more physically tangible interpretation of the numerical BEM results.

Using EEM, the surface charge distribution obtained from the retarded BEM calculations (which are in good agreement with the experiments) can be expanded in terms of plasmon eigenmodes of the trimer system (as they provide an orthogonal basis). [15] In Figure 5.11c these (normalised) amplitudes of such expansion are plotted for an excitation at the 614 nm resonance of the trimer assembly. It can be seen that only a few



Figure 5.11: Calculation results for electric fields and surface charges of an AuNP trimer: a) Local electric field enhancement map at the centre plane of the trimer for an optical excitation of the longitudinal resonance (614 nm excitation wavelength, calculated by retarded BEM). Disks indicate the particle positions. b) Surface charge distribution of the trimer for the same excitation as in a). c) Contributions of the first 100 eigenmodes to the longitudinal resonance feature of the trimer. Heights indicate the relative amplitudes of the different modes with the sum of all modes being normalised to 1. Surface charge distributions are depicted for the five most intense modes.

eigenmodes have a significant contribution to the resonance, the main one corresponds to the lowest-energy eigenmode (Figure 5.11c, highest bar): this mode is characterized by having a strong dipolar character, with a dipole moment aligned to the axis connecting the particles. [191, 192]

Within the EEM, the origin of this eigenmode (m = 1) can be approximately described by considering only nearest-neighbour interactions between nanoparticles. Accordingly, the interaction matrix (Section 2.3.1), which describes the localized plasmon resonances of the trimer, is of the form: [15, 154, 193, 194]

$$\mathbb{C} = \begin{bmatrix} 1 & C_{12} & 0 \\ C_{21} & 1 & C_{23} \\ 0 & C_{32} & 1 \end{bmatrix}$$
(5.1)

where  $C_{12} = C_{21}$  is the coupling coefficient describing the evanescent interaction between the 20 and 30 nm particle and  $C_{23} = C_{32}$  the coupling between 30 and 50 nm particle in dipole approximation. [195] Given the geometry of the assembled trimers it is  $C_{12} > C_{23}$  $(s_1 < s_2$  (Figure 5.1), Equation 2.37 and the highest dipole moment at the smallest particle (Figure 5.11c)).

The surface plasmon eigenmodes of the trimer are the eigenvectors of  $\mathbb{C}$ . The eigenvector corresponding to the lowest energy bright mode (m = 1) is given by (not normalised):

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} C_{12}/C_{23} \\ (C_{12}^2 + C_{23}^2)^{0.5}/C_{23} \\ 1 \end{bmatrix}$$
(5.2)

where each entry represents the contribution of a dipolar localized surface plasmon from each particle to the plasmon eigenmode of the trimer. The plasmonic lensing effect of the trimer is described by the fact that most of the excitation is localized between the two smallest particles (given that  $C_{12} > C_{23}$  i.e. stronger coupling between 20 and 30 nm particle than between 30 and 50 nm particle,  $a_3 < a_1 \& a_2$ ). The lensing effect within this level of approximation originates from asymmetric coupling among the nanoparticle trimer, which consequently leads to a dominant eigenmode characterized by a strong localization of the electric field in the gap between the two smallest particles.

As some trimers are not linear but rather in an angled arrangement, the impact of this bending on the plasmon modes was investigated. It was found that the contributions of the relevant eigenmodes do not change significantly (when staying below 55° bending angle) and the field enhancement map (lensing) is maintained (see Figure 5.12). This is consistent with previous observations. [196]



Figure 5.12: Influence of the bending angle of a trimer on its calculated (BEM) response to optical excitation. a) Calculated absorbance spectra for a linear (solid green), 27.5° bent (dotted) and 55° bent (dashed) trimer with a slight decrease of the longitudinal resonance peak intensity. A slight blue shift is also visible, as addressed before. The 20-30 nm dimer absorbance is given for comparison (blue). Bending angle ( $\alpha$ ) measured as depicted in b). b) Local field enhancement map calculated for a 55° bent trimer for non-polarised optical excitation at 610 nm . As with the linear configuration, the highest field enhancement is measured in the gap between the 2 smallest particles.

#### 5.5.3 Excitation with an Electron Beam

The measurements presented so far have addressed the response of an ensemble of trimers to optical excitation, whereas the theoretical considerations were focused on individual trimers. It is therefore essential to perform measurements on individual trimers, to better correlate the experiment with the theory and get experimental information about the spatial distribution of the different plasmon modes within one trimer. [197] This information provides insight in the predicted lensing capabilities of the trimer. Due to the high density of trimers implicit with our self-assembly method, dark-field optical spectroscopy is not possible as it would require beam focusing below the diffraction limit. Cathodoluminescence and electron energy loss spectroscopy are therefore utilised.

As both techniques use an electron beam as excitation source, the required spatial accuracy in positioning for probing the plasmonic lensing effect is provided. The electron beam acts like a localized broad-band point source and excites resonant modes in the nanostructure with an efficiency that depends on the electron trajectory with respect to the symmetry of the object. [54,198–200] In the case of CL, the excited modes are detected via

the radiative decay of the collective surface plasmon resonance. [201] In EELS, the excited modes perpendicular to the beam direction are detected by measuring the energy losses experienced by the electron beam. These two techniques are complementary, as depending upon the instrumentation used, CL typically offers superior energy resolution but inferior spatial resolution relative to EELS. [202–204]

Similar to the UV-vis measurements, retarded BEM calculations for CL (Figure 5.13) and EELS (Figure 5.14) spectra were used to provide insight into the localization of the different plasmon modes. This helped to interpret the experimental results for the electron beam impinging at different positions on a single trimer. Additionally, the (from the measurements independent) calculations allow for a verification of the accuracy of the applied model.

#### Cathodoluminescence Spectroscopy

Figure 5.13b and c show CL spectra with beam positions on the 20 and the 50 nm particle, respectively. The beam positions are indicated in the SEM images on the right. When the beam is centred on the 20 nm particle (Figure 5.13b), two main features are visible in the spectrum that were fitted with Lorentzians: A dominant resonance at around 1.77 eV and a smaller resonance at 2.06 eV. When the beam is positioned on the 50 nm particle (Figure 5.13c), the lower energy feature is suppressed below the detection limit and a single resonance at 2.15 eV remains.

In the following, the measured CL spectra are compared to those obtained by the BEM calculations (Figure 5.13a) to assign the observed peaks to longitudinal and transversal plasmon modes. For the beam position on the 20 nm particle, the calculated CL signal shows only one clearly visible resonance at  $\sim 2.02 \text{ eV}$  (614 nm). The additional higher energy resonance visible in the CL experiments is attributed to the wide beam of the SEM. This beam size leads to the excitation of additional modes and was not taken into account in these simulations. There is also an obvious redshift in the experimental data. Such energy differences between theory and experiment have previously been attributed to a thin dielectric shell (ligands and carbon coating in our case) and substrate effects. [204–206]

When the beam is positioned at the opposite side of the trimer (on the 50 nm AuNP), the low-energy resonance is still visible but with a greatly reduced intensity in the calculations. Due to the low signal to noise ratio this reduced lower energy feature cannot be identified in the experiment.



Figure 5.13: Electron beam excitation of plasmon modes of a trimer: a) Calculated CL spectra for different electron beam positions. Beam positions are indicated in the scheme on the right. b) Measured CL spectrum with the electron beam positioned on the 20 nm AuNP (see corresponding SEM image on the right). Green dots indicate the measured data while the solid green line represents the fitted spectrum consisting of two Lorentzians (dashed and dotted grey lines) c) Measured CL spectrum for an electron beam centred on the 50 nm AuNP (see corresponding SEM image on the right).

The calculated frequency of ~ 2.31 eV (537 nm) of the higher energy mode matches the resonance frequency of a single 50 nm AuNP and also the transversal mode observed with the optical excitation. The transversal character can be further supported by the increase of the calculated signal when moving the excitation source from the centre of the 50 nm AuNP to its off-axis side (Figure 5.13a, blue). A transversal mode can be excited more efficiently at this position than at the particle centre. [54,192,207] Similarly, the longitudinal character of the low energy mode is supported by its visibility for both on-axis excitations in the calculations (Figure 5.13a, green and orange).

By comparing the peak positions of the higher energy resonances in Figure 5.13b and c (orange), one can observe that the peak in Figure 5.13b is redshifted. This can be explained by a slight accumulation of carbonaceous material deposited around the assembly while performing the line scan (as the scan was performed starting at the 50 nm particle). [192]

In summary, the CL measurements and calculations show results matching with UV-vis data and the developed theory. It can be seen that when placing the beam on the 20 nm AuNP, the lower energy resonance, which is responsible for the desired lensing effect, is excited almost exclusively, which further supports the lensing idea (as will be discussed below).

#### Electron Energy Loss Spectroscopy

To map the different plasmon modes with a nanometre resolution, EELS measurements on a trimer were performed and the results are shown in Figure 5.14. Refer to Section 3.2.2 for more technical details on the EELS setup and the energy resolution limitations.

Similar to UV-vis and CL measurements, two main peaks can be identified: one above and one below 2 eV. Due to the high spatial resolution, the intensity of the lower energy component (which was attributed earlier to the relevant longitudinal resonance) can now be plotted for the different beam positions. This results in the map shown in Figure 5.14d which is in excellent agreement with the calculated EELS map. The map further confirms that the low energy resonance can most efficiently be excited at the smallest particle of the trimer, more specifically at the tip of the trimer structure. This is in good agreement with the CL measurements and the theoretical considerations presented above (also Equation 2.32 and 5.2). In contrast to the CL measurements, the expected (weak) excitation of the low energy mode at the edge of the 50 nm particle can also be observed providing further evidence for its longitudinal character.



Figure 5.14: Electron beam excitation of plasmon modes of a trimer: a) Calculated electron energy loss probabilities for different beam positions of a trimer structure as depicted in the annular dark-field scanning TEM (STEM) image in b) with a schematic indicating the beam positions. (Scale bar 25 nm) c) Principal component analysis components of the EELS data corresponding to the lower energy resonance of the trimer. d) Experimental and calculated loss maps for the lower energy resonance. e) and f) Similar to c) and d) but for the higher energy resonance. (Scale bar: 100 nm)

While a direct imaging of the plasmonic hotspot associated with the lensing effect is not possible with neither CL nor EELS, the strong agreement between the presented data and its theoretical description provides strong evidence for the nanolensing capabilities of the self-assembled trimers. It is important to emphasize again that neither CL nor EELS produce direct maps of plasmonic hot-spots. It has been noted in literature that when exciting with an electron beam, one may "be blind to hotspots" that occur in the space between adjacent nanoparticles. [198,208] On the contrary, it is possible to excite the resonances responsible for the plasmonic lensing, when the electron beam is positioned away from the associated hotspot. [208] The data of Figures 5.13 and 5.14 shows that this position is located at the tip of the trimer, while the plasmonic lensing hotspot is located in the gap between the two smallest particles.

### 5.5.4 Surface Enhanced Raman Spectroscopy

As mentioned before, a very popular application for plasmonic nanostructures with defined hotspots is SERS for molecular sensing. Therefore, a brief SERS study was undertaken with the as presented nanolenses. Three different substrate types will be compared in the following: The nanotrimers, the 20-30 nm dimers and a purchased Renishaw Klarite<sup>TM</sup> SERS substrate. Prior to the SERS measurements, the substrates were functionalised with



Figure 5.15: Surface enhanced Raman spectra for different substrates (vertical scale bar: 10000 counts). The different spectra are vertically offset to allow for clearer examination of each spectrum.

benzenethiol as a model analyte which is commonly used for such experiments. [115, 129,

209] More details on the experimental process are given in Section 3.5.

Figure 5.15 shows the resulting Raman spectra for the different substrates, a bare (i.e. without benzenethiol) trimer substrate is given for comparison. The most pronounced peaks commonly associated with the presence of benzenethiol are marked accordingly. [210] It is immediately visible that the by far highest raman signal results from the trimer assembly, which had to be expected. The commercial substrate did perform similar to the dimer assemblies.

While this is an encouraging result, some care has to be taken when interpreting it. As the analyte loading was only performed on the final assemblies, there would be more analyte on the trimer structures than on the dimer ones (as there are the 50 nm particles as additional surface area). Furthermore, there is an additional hotspot between the 30 and 50 nm particles that has to be taken into account. These issues could be mitigated by solely functionalising the 20 nm particles with a suitable analyte. This was, however, not done here as the SERS experiments were not used to draw conclusions on the lensing effect (more suitable methods have been used and presented for that) but rather to briefly showcase an application for the final substrates. This will be further elaborated in the outlook in Section 7.1.4.

# 5.6 Concluding Remarks

# 5.6.1 Discussion of the Inter-Particle Gap Size

One other point that needs some final discussion and had not been discussed in detail before is the gap size between the nanoparticles of an individual trimer ( $d_1$  and  $d_2$  in Figure 5.1). In order to achieve a self-similar arrangement as suggested in literature, those gaps would have to be tuned as well (although Li et al. show that exact self-similarity is not crucial). [38] While the gap sizes are not deliberately controlled in the approach presented in this chapter, a larger gap between the two larger particles ( $d_2$ ) was still expected. The smaller gap size of  $d_1$  compared to  $d_2$  can be rationalized based on particle curvature and the length of the DNA strands, compared to actual gap size and contact area between particles. Given that the DNA strands are much longer (> 10 nm) than the gap sizes, it seems that upon drying of the substrates, the gap size is merely defined by the amount of molecules in the gap (as they get squeezed together). Due to the higher curvature of smaller particles compared to bigger particles, this leads to less molecular mass being confined in the gap between the 20-30 nm AuNPs than between the 30-50 nm particles. That leads to a (on average) smaller gap  $d_1$ , as confirmed by the UV-vis measurements.

This is, however, only an average value. The actual gap sizes might vary between individual assemblies due to the faceted nature of the nanoparticles used for the assemblies. This effect had been studied before. [188,211,212] To determine how different gap sizes would affect the expected lensing effect and the expected measurables, calculations were performed for a trimer with  $d_1 = 1.7$  nm and  $d_2 = 1.1$  nm. As can be seen in Figure 5.16a, such a (no longer remotely self-similar) structure would have its hotspot in the gap between the two larger AuNPs. However, the UV-vis (b) and EELS (c) data that would be expected from such an assembly no longer match with what has been measured in the experiments. This further supports the gap size estimation presented above.



Figure 5.16: BEM calculations for a "reversed" setup:  $d_1 = 1.7$  nm and  $d_2 = 1.1$  nm. a) The resulting local field enhancement map with the hotspot between the two larger particles. b) Calculated EELS map for the longitudinal resonance. c) Calculated UV-vis spectrum with the actually measured resonance position indicated by the dotted line.

# 5.6.2 Summary

In conclusion, the electrostatic dimer assembly approach was successfully advanced to fabricate different trimer structures. DLVO theory was again utilised to develop the most feasible assembly strategy. The wet-chemical self-assembly process allowed the fabrication of nanolenses with sub 2 nm inter-particle gaps at high density at a macroscopic scale. High trimer yields of over 60% have been achieved. Finally, the strong plasmonic lensing effect of hierarchical gold nanoparticle trimers that has been at the focal point of theoretical studies for more than ten years could be demonstrated.

A characterization of the plasmonic properties by means of UV-vis, CL and EEL spectroscopy has been presented and matched with numerical BEM calculations. This enabled the identification of the lower energy resonance as a coupled longitudinal dipole mode, which is responsible for the strong lensing effect towards the gap of the smallest particles. More specifically, it could be demonstrated that this resonance can be efficiently excited when focusing an electron beam on the small particle supporting the idea of a strong localization of the electric field.

# Chapter 6

# Towards Other Particle Materials and Shapes

In this chapter the electrostatic assembly concept will be transferred to other nanoparticle materials and shapes. More specifically, heterogeneous nanoparticle dimers and trimers built from gold, silver and/or platinum will be looked at to show the transferability of the concept. After that, some advanced structures built of spherical and rod shaped nanoparticles will be presented in greater detail.



# 6.1 Replacing DNA

Before changing the nanoparticle material, a short experiment was undertaken to assess the effect of exchanging the surface functionalisation of the negatively charged particle (as thiolated single stranded DNA is economically not feasible for larger scale production applications). For this purpose, a functionalisation method presented earlier in literature was used to functionalise 30 nm AuNPs with thiol-PEG-sulfonate (TPS) molecules (see Figure 3.2b and Section 3.3.2, page 50). [95] The same thiol-chemistry was used to bind the molecules to the gold particles. The carbocylic acid group readily deprotonates at neutral pH and thus negative charge is confined on the particle surface. When using the same



Figure 6.1: Assembly results when replacing the DNA functionalisation with thiol-PEG-sulfonate (TPS). a) Core assembly of the TPs-AuNPs. b) Dimer assembly of 50 nm TMAC functionalised particles on the 30 nm TPS functionalised core particles. (scale bars: 500 nm)

assembly parameters as for the DNA-functionalised particles, a similar core assembly can be achieved with rather uniform nearest neighbour distance (Figure 6.1a). This core assembly can then be used to get the dimer assemblies as in the previous chapters (Figure 6.1b). One can see that there are still a few uncovered core particles after the dimer forming step. This had to be expected, as the assembly parameter were not optimised for the new (changed)  $\zeta$ -potential of the core particles due to the TPS. While this leads to lower dimer yield as shown before, it still proves the transferability of the concept and indicates that the particular surface functionalisation is not relevant, as long as the appropriate charge is confined on the particle surface. A further optimisation for these conditions was therefore not pursued.

# 6.2 Nanoparticles of Different Materials

All nanoparticles structures presented so far were assembled from spherical gold nanoparticles. However, in order to apply the developed electrostatic concepts to wider use, the feasibility of the method in combination with different nanoparticle materials needs to be shown. In the following, this will be done using silver as a material with reduced plasmon damping and platinum as a prototype catalytic material. [9,213–216]

# 6.2.1 Ag-Au Heterodimers

Citrate stabilised, colloidal 60 nm silver particles were used for dimer assemblies with 30 nm AuNPs. There are two options to form such hetero-dimers: Either the AgNPs could be used as core particle in the first assembly step or as satellite particle in the second step. Both possibilities were attempted.

A first attempt to load thiolated DNA on the AgNPs did not succeed, as the particle colloid was not stable in the presence of higher amounts of NaCl. The NaCl would have been necessary to achieve a high density of DNA strands on the particles during the functionalisation step. [217, 218] It was therefore decided to functionalise the particles with TMAC and use them as satellites, as this process does only require very low NaCl concentrations (see Section 3.3.4, page 53 for full protocol).



Figure 6.2: SEM images of gold-silver hetero-dimer assemblies. a) High resolution SEM micrograph of 60 nm AgNPs assembled on 30 nm AuNPs. Small fragments of the AgNPs are visible, as indicated with the white arrow (scale bar: 250 nm). Inset showing a zoom in on the arrow region. b) Overview SEM micrograph of the same assemblies (scale bar: 500 nm).

Figure 6.2 shows a typical result of an assembly of 60 nm TMAC functionalised AgNPs on 30 nm AuNPs. It is obvious that the yield could be further optimised by increasing the ionic strength, the temperature or the particle concentration of the assembly solution in the dimer forming step. A further optimisation was not pursued as the point of this experiment was not to achieve the highest possible yield but rather to show that a transfer of the concept to another particle material is possible.

Another notable observation concerns the AgNP stability. Smaller fragments of silver particles were observed in all assemblies, mostly attached to the 30 nm AuNPs. An example is indicated with the arrow in Figure 6.2a. These impurities can be traced to the AgNPs, as they are also visible when only AgNPs are assembled on a negatively charged substrate. In another case, the fragments can be seen around the AgNPs on the substrate (see Appendix D.1). It is, however, unlikely that the initial AgNP colloid is contaminated with smaller fragments, as those would be removed in the washing process (due to their smaller mass). Those fragments can thus be attributed to the lower stability of the AgNPs when compared to the AuNPs. This decomposition has been observed before for AgNPs on TiO<sub>2</sub> and had been attributed to plasmon induced oxidation and charge separation. [219] The assemblies seemed not to be greatly affected by those fragments (apart from their presence on the AuNPs).

Figure 6.3 shows a typical UV-vis spectrum of the resulting hetero-dimers. Several



Figure 6.3: UV-vis spectrum of an Ag-Au dimer assembly as shown in Figure 6.2. The orange dotted line indicates the position of the 30 nm AuNPs' plasmon resonance.

peaks can be identified: The highest resonance at  $\sim 430 \text{ nm}$  with a shoulder on its higher energy side, which is characteristic for the 60 nm AgNPs (Section 3.3.4, page 53). Furthermore, a resonance at  $\sim 530 \text{ nm}$  (indicated with the orange line) is visible, which had been observed in all previous experiments for the 30 nm AuNPs (e.g. Section 3.3.1, page 48). An additional resonance peak can be observed at  $\sim 565 \text{ nm}$ , which cannot be attributed to one of the two individual nanoparticle species. It therefore indicates the existence of a coupled resonance of the Ag-Au hetero-dimers (similar to the ones that had been observed for the AuNP dimers and trimers).

# 6.2.2 Pt-Au Dimers and Trimers

An alternative nanoparticle species that was used to produce hetero-dimers and -trimers was a colloid of citrate stabilised 30 nm PtNPs. This work was in parts done in collaboration with Philip Greubel and some of the results presented here were used for his Master's Thesis.

As with the gold and silver particles, it was possible to use thiol-chemistry to functionalise them with the appropriate molecules to confine the charges on their surface. Both assembly approaches were pursued for the PtNPs (i.e. they were functionalised to confine negative or positive surface charges) and in contrast to the AgNPs, both approaches were possible. The particle functionalisation protocol had to be adjusted for the PtNPs. The Zheng method for the DNA functionalisation was not possible in this case. [217]



Figure 6.4: SEM images of Au-Pt hetero-structures. a) Overview image of a high yield dimer assembly with 60 nm AuNPs and 30 nm PtNPs (scale bar: 500 nm). b) High resolution SEM micrograph of the same assemblies (scale bar: 100 nm). c) Overview image of a dimer assembly with 30 nm AuNPs and 30 nm PtNPs (scale bar: 500 nm). Inset: TEM image of a single Au-Pt dimer (scale bar: 30 nm). d) Trimer assembly attempt with 30-30-50 nm Pt-Au-Au particles (scale bar: 150 nm).

Figure 6.4 summarises the results for the assemblies with the PtNPs as negatively charged cores (a and b) and as positively charged satellite particles (c and d). For the 30-60 nm Pt-Au dimers, yields up to 88% could be achieved. This is comparable with what

Zheng et al. achieved for 30-60 nm Au-Au dimers and shows once again that the method is fully transferable if suitable surface functionalisation can be achieved. [55] When using the PtNPs as satellites with 30 nm AuNP cores, yields of up to 80% were achieved. Again the lower yield for similar sized core and satellite particles has been observed before. [55, 183] While it is not possible to distinguish the PtNPs from the AuNPs according to their size for those assemblies, they can be distinguished by their morphology. As can be seen in the TEM image (Figure 6.4c, inset), the PtNPs have a more polycrystalline structure, while the AuNPs are rather monocrystalline. This might also be a reason for the observed different behaviour during the surface functionalisation.

Finally, an attempt was made to produce nanoparticle trimers with the PtNP at the tip (Figure 6.4d). First results were promising, as can be seen in the SEM image. Similar to the gold trimers, linear and collapsed trimers could be observed. However, more optimisation would have been needed to achieve significant trimer yields. As this had proven rather time consuming for the gold trimer nanolenses, it was not further pursued (as it was not a central goal of the project). The experiments with the PtNPs have already shown that it is possible to use the electrostatic assembly concept to produce hetero-structures according to the AuNP prototypes. This is quite significant for various applications, as has been seen in the introductory chapter: The gold nanoparticles can be used to inject electrons in to the PtNPs and enhance their catalytic capabilities. But one could also think about combining a photo-catalyst with a co-catalyst this way (other than gold).

# 6.3 Combining Spherical Particles with Gold Nanorods

Up to this point, all nanoparticles used for the assemblies were spherical particles. This was done to reduce the relevant parameters for the electrostatic assembly process (as the orientation of an individual particle did not need to be taken into account due to symmetry). However, as shown in the introductory section (Section 1.2.4, page 9), the plasmonic properties of nanoparticles have a strong shape dependence. It would therefore be desirable to be able to exploit this with the here presented assembly approaches. So far, the only way to change the plasmonic properties was to vary the nanoparticle size or their arrangement. The next obvious step is now to break the central symmetry of the sphere in one direction. This can easily be done by using gold nanorods (GNRs). In the subsequent section, the electrostatic assembly options for a combination of GNRs with AuNPs will be investigated in detail.

The central idea for the assembly process remains the same as before: electrostatic interactions of charged particles and surface drive the stepwise assembly of dimers and trimers. [55, 174, 183]. However, as the nanorods are not centrosymmetric, it is now of interest to control the position of the other particle (AuNP) with respect to the GNR. More specifically, the assembly process should allow for specific positioning of the spherical particle at the tip (tip-on) or at the side (side-on) of the GNR. The ultimate goal is the placement of a spherical particle in the gap between two GNRs (Figure 6.5). [81,220]



Figure 6.5: Schematic of the assembly patterns that are produced by the here presented strategy: a) The spherical particle at the tip of the rod (tip-on), b) at the side of the rod (side-on) or c) in the gap between two rods (in-gap).

# 6.3.1 Tip-On Particle Assembly

# The Idea

The idea for the tip-on assembly is identical to the now well known dimer assembly approach: Using a positively charged substrate, negatively charged core particles in the first

assembly step, and positively charged GNRs as satellites for the second step. The core particles act again as adsorption sites for the satellite particles and an electrostatic funnel is expected to form. However, the situation is now different, as the GNRs will experience a different repulsive or attractive force depending on their orientation. This is indicated in Figure 6.6. The hypothesis was that a rather upright orientation of the GNRs during



Figure 6.6: Schematic of the two principally different adsorption orientations of the GNR (positive and negative charges indicated in green and red, respectively). a) Upright, possibly equilibrium position. b) Horizontal orientation of the GNR with strong interactions between the positive charges on GNR and substrate (arrows). c) Drying process of the upright adsorbed GNR.

the assembly process would allow for minimisation of the overall interaction energy. In the upright position, most positive charges of a GNR would be "shielded" from the positive charges of the substrate by the negatively charged core particle. Assuming a rather horizon-tal adsorption would lead to a rather strong repulsive force between the positively charged substrate and the GNR (as illustrated in Figure 6.6b, arrows indicating the conflicting charges). According to this hypothesis the upright position during the assembly process would then lead to the desired tip-on assembly conformation upon drying (Figure 6.6c).

# First Tests

A feasibility test for the tip-on assembly was done with the standard DNA-functionalised 30 nm AuNPs used in the previous studies. A first indication was already given by occasional impurities in the 50 nm particles: During the dimer assembly experiments it was observed that whenever there were rod-shaped impurities in the satellite colloid, they would assemble in a tip-on configuration (Figure 6.7a and b)

To allow for the highest possible interaction energy (and ideally a narrow electrostatic funnel), the initial experiments were conducted without any NaCl addition in the satellite assembly solution. Different GNR particle concentrations were tested and a representative SEM image of a high dimer yield assembly can be seen in Figure 6.7c (see appendix D.2 for overview SEM image). Several observations can be made from these results: Firstly,



Figure 6.7: a) TEM image of a nanorod impurity assembled to a 30 nm AuNP core. (scale bar: 50 nm) b) SEM image of a similar assembly. (scale bar: 50 nm) c) SEM image of GNRs assembled as satellite particles on negatively charged 30 nm AuNPs. Tip-on and side-on assembly geometries can be observed. (scale bar: 250 nm)

the dimer assembly concept is easily transferable to non spherical particles. The absolute dimer yield is as high as 74%. Secondly, while there seems to be indeed a preferred tipon adsorption geometry, other geometries are frequently observed as well. However, a possible reason for that can be identified when comparing these assemblies to the ones in Figure 6.7a and b: The nanorods used for the assembly in c) have a diameter significantly smaller ( $\sim 20 \text{ nm}$ ) than the 30 nm core AuNPs they adsorb on. The relatively large particles mostly shield the GNRs from the repulsive substrate and thereby hinder a more pronounced preference for a tip-on assembly geometry.

#### Switching to 20 nm Core Particles

From the initial hypothesis, it can be seen that a smaller core particle should lead to a larger difference in energy between the two adsorption geometries and *vice versa* (as a smaller particle would provide less shielding from the substrate; Figure 6.6). 20 nm particles will therefore be used as core AuNPs from here on.

As so far only 30 nm were used as core particles, the assembly conditions to achieve a uniform nearest neighbour distance with the 20 nm particles had to be determined first. An assembly solution with optical density 0.07 was determined to give the best results (Figure 6.8), further concentration did not yield significant changes. When lowering the concentration, the nearest neighbour distance can be increased, however, the uniformity of the distribution is not maintained.



Figure 6.8: Histograms of the nearest neighbour distances  $d_{nn}$  of 20 nm core particle assemblies when using different nanoparticle concentrations in the assembly solution: a) Optical density: 0.07, b) optical density: 0.05, c) optical density: 0.03, d) optical density: 0.01. The total particle count for each histogram and the mean values are given in the plot.

#### The Final Tip-On Assembly

With the new core particle assemblies, it was then possible to proceed again with the tipon strategy. As the repulsive interactions between the rods and the substrate were to be used to drive a tip-on configuration, the initial parameters to optimise the yield of correct assemblies did not involve the addition of NaCl to the assembly solution. It would allow for a higher dimer yield but it would do so by shielding the repulsive substrate surface charges.

Firstly, the influence of the GNR particle concentration in the assembly solution was was investigated. It was found that (similar to the experience with the spherical particles) a large excess of satellite particles was needed to reach higher dimer yields (compared to the available cores as adsorption centres). As can be seen in Figure 6.9a for assemblies at 25 °C with no NaCl added to the solution, the desired tip-on configuration could be increased from  $\sim 13\%$  to 19%. This was achieved by increasing the optical density of the assembly solution (i.e. the GNR concentration) from 0.4 to 1. An even higher concentration did not have an effect on the tip-on dimer yield, however, an increased nonspecific adsorption of GNRs on the substrate could be observed.

Secondly, the assembly temperature was increased. Again, as expected, a higher temperature facilitated the dimer formation during the assembly as is shown in Figure 6.9b.



Figure 6.9: The dependence of the assembly results on a) the GNR concentration in the assembly solution and b) the temperature of the assembly solution. The different observed structures are indicated with pictograms. The same legend is used for a) and b). The percentage of the core particles without a GNR attached is not shown here, as it is out of scale (70-80%). Smaller percentages are not labelled for the conditions that were not further used.

By increasing the temperature to 40 °C it was possible to achieve a 27% tip-on trimer yield.

The effect of the incubation time was not studied in greater detail as only a slight increase of 2% could be detected for the tip-on assemblies when increasing the incubation time from 3 h to 5 h.

While it is possible to increase tip-on dimer yield by adjusting the above presented parameters, the overall yield remains low. Therefore the ionic strength was adjusted in a next step and showed the largest impact on the assembly yield. These experiments were done at a GNR optical density of 1 and at 30 °C (while higher temperatures had shown a better yield, they led to instabilities when NaCl was added). Different NaCl concentrations were used and the results are shown in Figure 6.10. It is noteworthy here that the optimised NaCl concentration for the GNRs was ~5 times higher than for 50 nm spherical AuNPs. Besides the steep increase of the tip-on dimers with the increased NaCl concentration, a larger amount of agglomerates can be observed as well. Agglomerates are defined as all multimers that comprise more than one AuNP and one GNR. This is consistent with the model of the electrostatic assembly, as the higher ionic strength of the assembly solution decreases the adsorption barrier. The best compromise with a high dimer yield and still low agglomerate amounts was found for a 115  $\mu$ M NaCl concentration resulting in a 73%<sup>1</sup> yield of tip-on dimers.

In summary, the starting hypothesis can be regarded as confirmed, as  $\sim 78\%$  of the

<sup>&</sup>lt;sup>1</sup>The yield has been corrected for cubic impurities in the initial GNR colloid.



Figure 6.10: a) The dependence of the assembly results on the NaCl concentration in the assembly solution. Small percentages are only labelled for the best assembly condition. b) SEM image of an optimised tip-on assembly. (scale bar: 400 nm)

spherical AuNPs are located around the tips (tip-on and tip-side conformation) of the GNRs. Only 5.8% of the particles are found in a side-on position.

# 6.3.2 Side-On Particle Assembly

After controlling the positioning of the AuNP at the tip of the GNR, the next step was the controlled positioning on the side. To achieve this, a reversed assembly approach as illustrated in Figure 6.11a was chosen. If successful, this would also rule out an alternative interpretation of the results observed in the tip-on assembly: A tip-on assembly geometry would also be expected if the GNRs were not uniformly coated with TMAC but rather selectively at the tips (which is possible due to the different crystal facets [221], Figure 6.11b).

In order to perform the reverse assembly, the SiO<sub>2</sub>/Si substrate did not need to be functionalised with APTES, as it already has a negative  $\zeta$ -potential at neutral pH (Section 3.3.7, page 54). In the first assembly step, the substrate was exposed to a TMAC functionalised GNR colloid (OD = 1) for 2 h at 30 °C. The GNRs readily adsorb on the substrate and form a uniform assembly similar to the one with the AuNP cores (Figure 6.12a).

After blow-drying, the substrate is then exposed to a colloid with DNA functionalised 20 nm AuNPs in a consecutive step (OD = 0.35, T = 25 °C, t = 3 h). Those negatively charged AuNPs are expected to adsorb in a central on-top position as shown in Figure 6.11a, step 2 (for uniformly coated GNRs). This is caused by the repulsive interaction with negatively charged substrate which gets minimised in the central, on-top position.



Figure 6.11: a) Basic concept of the reverse assembly approach: In the first step, the positively charged GNRs are assembled on the clean (negatively charged)  $SiO_2/Si$  substrate. In the second step, the negatively charged core particles are then assembled using the rods as adoption centres. b) Alternative model that would lead to similar results as observed in the tip-on assembly: A facet dependant selective coating with the TMAC molecules only at the tips of the rods. This would also lead to a tip-on assembly for the reverse approach.

After dip-washing and vertical drying, the assembly pattern shown in Figure 6.12b can be observed. Note that the NaCl concentration in step 2 was again optimised (to a 0.4 mM concentration) following the same procedure as outlined before.



Figure 6.12: a) SEM micrograph of the GNR assembly on  $SiO_2/Si$  after step 1. (scale bar: 200 nm) b) SEM micrograph after the 20 nm AuNPs were added in step 2. (scale bar: 200 nm) c) Statistics of the different observed structures after step 2. The green colors indicate the side-on assemblies that were the assembly goal, orange are tip-on assemblies and other mono- and multimers are summarised in blue.

As can be seen in Figure 6.12b and c, the majority of the spherical particles (~ 86%) is indeed adsorbed at the side of a GNR rather than the tip<sup>2</sup>. This is consistent with the hypothesis of the assembly strategy and proves that rather precise control over the adsorption geometry is possible: Only a minor percentage of the particles adsorbed in a tip-on position. The percentage of nonspecific adsorption and multimers was low as well.

It is notable here that 30% of the observed structures are GNRs with the AuNP still

<sup>&</sup>lt;sup>2</sup>Corrected for the non-rod-shaped impurities in the initial colloid again.

sitting on top. They did not get dragged down during the drying process, as has been observed for small satellite particles in the previous chapter. It was found that this drying behaviour can be controlled to a certain degree as well. By drying the substrates after step 2 under a stream of nitrogen (rather than slowly drying it vertically on air, see Section 3.4) the samples dry within seconds and a large percentage of the AuNPs remains in a ontop position (as can be seen in Figure 6.13). At the same time, a reduced percentage of



Figure 6.13: a) SEM micrograph of a reverse assembly (rods first, then spherical particles) that underwent a nitrogen blow-drying after step 2. (scale bar: 200 nm) b) Statistical analysis of an assembly as seen in a).

multimers and tip-on assemblies can be observed. Blow drying test for the tip-on assemblies had already suggested that those structures are easily destroyed by the harsh conditions of the fast drying method.

#### 6.3.3 In-Gap Assembly

With the control over the assembly geometry of one AuNP and one GNR accomplished, the last goal was the placement of an AuNP between the tips of two GNRs (a geometry used by e.g. Aouani et al. [81]). To fabricate such structures using only electrostatic assembly, the same approach as for the AuNP trimers in Chapter 5 was used: The dimer assembly is extended to a trimer by adding another satellite particle. Applied to the GNRs that means that after performing a tip-on assembly with the negatively charged AuNPs and the positively charged GNRs, another rod is added in the third step (Figure 6.14a). Similar to the AuNP trimer, the second rod is expected to adsorb in a position furthest away from the first one and thus to produce the desired structure.

This behaviour could be observed as can be seen in Figure 6.14b and  $c^3$ . The majority of the observed structures (69%) comprises one AuNP and two GNRs, however, some of those

<sup>&</sup>lt;sup>3</sup>The statistics are again corrected for non rod-shaped impurities in the GNR colloid.



Figure 6.14: a) Scheme of the assembly pathway: tip-on assemblies are extended to trimers by adding a second GNR to it. Surface charges: green = positive, red = negative. b) SEM micrograph of a trimer assembly with the goal to have an AuNP in between the tips of two GNRs. (scale bar: 200 nm) c) Statistical analysis of the trimer assembly. The blue part indicates agglomerates and isolated nanoparticles or rods found on the substrate.

are strongly bent ("collapsed") or have at least one GNR adsorbed in a side-on geometry. This had to be expected as some side-on adsorption has already been observed for the dimer-forming step. 42% of all structures were the trimers with a tip-on arrangement for both GNRs and a bending angle of less than 90°.

The major cause for the lower yield of the correct trimer structures is given by the assemblies that stay in a dimeric form (32%). An increased ionic strength of the assembly solution could not mitigate this problem as it led to an increased amount of agglomerates and unspecific adsorption. A potential reason for the high amounts of dimers is the high overall density of particles on the surface that present a significant repulsive potential for the particles in the third assembly step. As the AuNPs are smaller than in Chapter 5 (20 nm instead of 30 nm), they provide less attractive force to overcome this barrier. This was already apparent from the high ionic strength needed for the AuNP-GNR dimer assemblies.

# 6.4 Summary

In this chapter, the electrostatic assembly approach was developed further from the previously used AuNPs. By using different particle materials and a different surface coating ligand for the negatively charged particles, it was possible to show that the assembly strategy is a very general concept that could be applied in various fields.

More importantly, the assembly method could be applied to non-spherical particles. It was possible to fabricate dimer and trimer structures consisting of spherical and rod-shaped gold nanoparticles with up to 94% yield. The so assembled structures are highly relevant for applications (as has been shown in the introduction) and are the proof that a precise control over the positioning of the nanoparticles relative to each other can be achieved by the simple electrostatic concept. Furthermore, the observed assembly behaviour offers the opportunity for a new kind of sensors as will be shown in the outlook in the next chapter.
## Chapter 7

# **Outlook and Conclusion**

This last chapter will give an outlook and a summary of the key findings of the thesis, pointing out their relevance in different research areas. In order to show the possibilities for future application of the here presented research, some more preliminary results will briefly be presented in the outlook section. For this reason, the final concluding remarks will be given after the outlook section.

### 7.1 Outlook

The following outlook section will briefly discuss some preliminary results for other applications of the electrostatic self-assembly and introduce some ideas for future projects involving the research presented here.

#### 7.1.1 Gold Nanoparticles on Patterned Substrates

The electrostatic assembly of AuNPs on substrates for further use in catalysis was briefly explored. This work was done in collaboration with the Catalonia Institute for Energy Research (IREC). The gold nanoparticles were assembled on silicon chips with etched channels, as have been presented by Dávila et al. (Figure 7.1a). [222] In order to use such chips for thermoelectric energy harvesting, silicon nanowires are required in the trenches. This is commonly done by catalytic nanowire growth (catalysed by gold particle seeds). As such, the electrostatic assembly method was a desirable technique, as it produces gold seeds with uniform size and spatial distribution. Conventionally used methods like evaporation



Figure 7.1: a) Schematic illustration of the basic structure of the thermoelectric device (grey: Si, blue: SiO<sub>2</sub>, yellow: W). (© 2012 Elsevier) [222]. b) Overview image of the trenches in a silicon chip designed for a thermoelectric device (scale bar:  $50 \,\mu\text{m}$ ). c) Close-up SEM image of one trench wall with electrostatically assembled AuNPs attached to it (scale bar:  $2 \,\mu\text{m}$ ). d) Silicon nanowire grown with the AuNPs as seeds (scale bar:  $4 \,\mu\text{m}$ ).

of a thin Au layer and subsequent annealing fail to produce layers with a similar uniformity. [77,223] Furthermore, such techniques face difficulties when it comes to non-planar substrates (as the here presented ones).

As can be seen in Figure 7.1b and c, it was possible to assemble the AuNPs on the vertical walls of the channels. The seeds were then used for catalytic nanowire growth as seen in Figure 7.1d. In the future, dimer assemblies might be used to assemble nanowire seeds next to a co-catalyst particle or a doping material.

#### 7.1.2 Transfer to Any Substrate

A transfer process for the nanoparticle assemblies was trialed in collaboration with Dr. C. Ng. For further experiments, it was necessary to deposit evenly distributed GNRs on a layer of TiO<sub>2</sub> or even embed the GNRS in the TiO<sub>2</sub> layer. To achieve this, the GNRs were electrostatically assembled on a layer of methyl methacrylate (MMA) according to the standard procedure for glass substrates. The assembly results were identical to the ones obtained on SiO<sub>2</sub>/Si (Figure 6.12a, page 116). Through subsequent evaporation of TiO<sub>2</sub>, the addition of a supporting substrate and dissolution of the MMA layer, the GNRs could successfully be transferred (Figure 7.2).



Figure 7.2: Schematic of the assembly and transfer process: a) GNRs are electrostatically assembled on a Si wafer with an MMA layer on top. b) A 50 nm TiO<sub>2</sub> layer is deposited on the assembly via electron beam evaporation. c) A supporting glass substrate is attached using an epoxy adhesive. d) The MMA layer is dissolved to release the structure from the Si wafer. e) SEM image of successfully transferred GNRs embedded in the TiO<sub>2</sub> surface (scale bar: 500 nm).

These experiments demonstrate two key findings that extend the potential of the technique: The assembly can be scaled up (the substrates used here measured  $10 \times 20$  mm) and they can be transferred to basically any planar substrate. Further studies are required to also prove that for the more complex assembly structures. If successful, the assemblies on MMA mitigate the optimisation step of the assemblies for new substrates, as they could simply be transferred from the MMA.

#### 7.1.3 Electrostatic Assembly of a Lithography Mask

Another application of electrostatic assembly was explored with the assembly of polystyrene spheres (PS) on a layered structure with TiO<sub>2</sub> as topmost layer. The goal here was the fabrication of electrodes for back-contact perovskite solar cells. [224, 225] The PS were hereby used as lithography masks. A schematic of the process can be seen in Figure 7.3. The PS (1  $\mu$ m diameter) had a negative  $\zeta$ -potential (-92±5 mV) due to surface carboxy-



Figure 7.3: Schematic fabrication process of a back-contact solar cell electrode with electrostatically assembled lithography mask: a) The conductive glass with the hole transport layer is functionalised with APTES to allow for electrostatic particle assembly. b) The substrate is incubated in a colloidal solution of negatively charged polystyrene spheres (PS). c) The PS assemble in a dense monolayer as can be seen in the SEM image in d) (scale bar:  $4 \mu m$ ). e) After annealing, the PS are shrunk by an air plasma treatment. f) SEM image of the resulting structure (scale bar:  $4 \mu m$ ). g) Subsequent gold evaporation and PS lift-off leads to a microstructured gold electrode as shown in h).

late groups, which allowed for a electrostatic assembly on the positively charged, APTES modified  $TiO_2$  (Figure 7.3a and b). APTES functionalisation was done according to the standard protocol (Section 3.3.7, page 54).

In contrast to the research shown so far, a rather densely packed monolayer of the PS was required. This was achieved by increasing the ionic strength of the assembly solution and thus reducing the repulsive interactions between individual spheres. The resulting assembly pattern can be seen in Figure 7.3c and d. In order to use the so produced pattern as a lithography mask, the spheres were further fused to the surface by an annealing step and subsequently shrunk by air plasma treatment (Figure 7.3e and f). After evaporating gold (Figure 7.3g), the PS could then be dissolved, leaving a perforated gold layer on the substrate (Figure 7.3h). The so produced electrodes were then further used to fabricate back-contact pervoskite solar cells. The use of the self-assembled mask results in a robust and cheap fabrication process that doesn't require sophisticated equipment (as opposed to photolithography).

#### 7.1.4 Switching the Trimer Nanolenses On

As mentioned earlier in Chapter 5, the trimer nanolenses have a big potential for sensing applications. The main reason for that is the high plasmonic field enhancement in the gap between the two smallest particles. But while large field enhancements that can be utilised for e.g. SERS can be found with other structures as well, the trimer structure has a rather unique advantage: the fluorescent molecule or SERS analyte can be locally separated from the target molecule<sup>1</sup>.

This can be done by a measurement setup as shown in Figure 7.4. The fluorescent



Figure 7.4: Schematic representation of how a fluorescent signal can be "switched on" with the trimer assembly. a) The starting point for such a sensing experiment is the 20-30 nm dimer (positive and negative charges are indicated with signs). The 20 nm particle would carry a fluorescent molecule. This trimer could then either be exposed to the target molecule (indicated in blue, b) or not (c). In the first case, the trimer formation would be prevented (see zoomed region), in the later case, the trimer formation would lead to a fluorescent signal due to the enhanced light focusing.

molecules (absorbing at the longitudinal frequency of the trimer) would be confined on the 20 nm AuNPs prior to assembly. Once the 20-30 nm dimers are formed, the fluorescent signal would still be weak. The signal would only be "switched on" upon adsorption of the 50 nm AuNPs to complete the trimers, thus effecting the large field focusing. As this trimer forming step is quite sensitive to experimental conditions (such as the particle surface charge), suitable chemistry could be used to prevent trimer formation in the presence of the target molecule.

#### 7.1.5 Tip-On GNR assemblies as Flow-Sensor

In Chapter 6.3.1 it was hypothesised that the GNRs would be oriented in a rather upright position upon adsorption on a 20 nm core particle during the tip-on assembly process

 $<sup>^1\</sup>mathrm{The}$  target molecule here is the molecule that one seeks to detect

(Figure 6.6, page 111). The experiments supported this hypothesis. Besides the desired tip-on assembly, this assembly step could be utilised to build a microfluidic flow sensor and potentially map the flow of a fluid on nano-scale. To do so, one would utilise the different plasmon modes that can be excited in the GNR-AuNP dimer (Figure 7.5a). The



Figure 7.5: Schematic idea of a microfluidic flow sensor based on the GNR assembly process: a) The transversal (dark blue) and longitudinal (green) mode of a coupled GNR-AuNP dimer can be observed at different wavelengths. The two different situations are illustrated with the electron cloud marked in bright blue. The E-field direction of the incident light is marked at the top. b) During the tip-on dimer assembly, the GNR is expected to be in a rather upright position (being repelled by the substrate). c) A flow of the liquid (blue) would lead to a modified position of the GNR.

transversal and longitudinal mode can be observed at different wavelength in the absorption spectrum. That way, it is possible to determine the orientation of the GNR with respect to the incident light. In the static situation, the transversal mode would be expected to be observed when illuminating from the top (Figure 7.5b). In the situation with a flow, the GNR is expected to be pushed in a more sideways orientation, which would lead to an increased excitation of the longitudinal mode (Figure 7.5c). This would allow for the detection of a flow at the location of the GNR, further information about the direction can be gained by adding a polariser in the light path.

### 7.2 Summary and Concluding Remarks

The here presented thesis was driven by the idea that in order to fabricate complex nanostructures, it should not always be necessary to apply overly complex fabrication methods. Additionally, this method should produce assemblies with a high yield, which would be necessary for future application beyond fundamental scientific studies. This idea led to the thesis objectives that comprised the full understanding of the electrostatic assembly process and its relevant parameters, its extension to trimer assemblies and the application to different particle shapes and materials. In order to achieve these objectives, the thesis was structured in three main parts, each addressing one or several of the initial milestones. The key findings of those parts will now be summarized.

#### 7.2.1 Understanding the Electrostatic Nanoparticle Assembly

After the preparation of the different building blocks, according to protocols presented in Chapter 3, Chapter 4 was dedicated to studying the electrostatic assembly process for the dimer formation. The influence of various assembly parameters was investigated in theory and also in experiment.

A computer program was written to implement the DLVO theory in a way that allowed for easy simulation of different assembly pathways. Using different experimental parameters, such as the size of the involved parameters,  $\zeta$ -potentials of the particles and substrate, ionic strength of the assembly solution and assembly temperature, it was possible to calculate interaction energies for different particle locations and to identify gradients driving the assembly. By comparing the calculations to experimental results, it became obvious that while already giving good advice for potential assembly protocols, the Maxwell-Boltzmann distribution needed to be considered as well.

This led to the development of a size selective assembly process which enabled the preferential adsorption of 20 nm AuNPs from a bidisperes solution of 20 and 50 nm AuNPs. Parameters such as incubation time and assembly temperature were used to improve the selectivity and it was possible to achieve a 28 fold increase in concentration of the 20 nm AuNPs on the surface when compared to the solution. While mainly paving the way for the development of the assembly protocols in the subsequent chapters, these findings may also have impact in the field of microfluidics and targeted sensing.

#### 7.2.2 Assembly and Investigation of Plasmonic Trimer Nanolenses

After identifying the crucial assembly parameters, the protocol was evolved to trimer formation. When the initial 50-30-60 nm trimers proved the feasibility of the concept, the process for the desired 20-30-50 nm trimers was developed. The optimised assembly protocol achieved a 63% overall trimer yield and the majority of those hierarchical trimers were classified as linear.

These sought after self-similar structures were then analysed in detail. UV-Vis measurements were used to investigate the average optical properties of such an assembly. The measurements were complemented with retarded BEM calculations, which showed the expected strong local field enhancement in the gap of the 20 and 30 nm AuNPs of a trimer. Using EEM expansion, the relevant eigenmode of the coupled system responsible for this focusing could be identified.

To further support the lensing idea, the plasmonic properties of individual trimers were studied by means of CL and EEL spectroscopy. Both techniques use an electron beam as probe, which allowed for a high spatial resolution. While this resolution was the highest for the EELS, the CL complemented the measurements with a higher resolution in frequency space. The so acquired data was compared to the BEM predictions for the CL and EELS data. The good match of theory and experiment strongly suggested that the calculated field enhancement maps (which could not be measured directly) were correct as well.

The optimised trimer assemblies were then used for SERS with benzenethiol as a model analyte. The intensity of the recorded Raman signals were compared to the ones from commercial Renishaw Klarite<sup>TM</sup> SERS substrates and the 20-30 nm dimer assemblies. It was found that the trimers produced a much higher signal than both other substrate types. Other experiments to further investigate and utilise this were suggested in the outlook section.

#### 7.2.3 Expanding the Technique to Other Particle Shapes and Materials

In order to improve the applicability of the electrostatic assembly approach to other fields, other particle materials and shapes were used. Among others, the technique proved to be easily transferable to the prototype catalyst material platinum, and heterogeneous dimer and trimer structures could be assembled with yields up to 88%. Such structures are interesting for photocatalysis where different co-catalysts (or gold for hot electron injection) need to be placed in close contact.

Gold nanorods were used for assemblies with 20 nm AuNPs and protocols for the precise placement of the spherical particles with respect to the GNRs were developed. Three different, defined arrangements were achieved: the AuNP at the tip of a GNR (73% yield), the AuNP at the side of the GNR (86% yield) and the AuNP in the gap between two GNRs (42% yield). Furthermore, modification of the drying process allowed control over the assembly of the AuNP on the side of a GNR: a N<sub>2</sub> blow-drying led to preferential assembly of the AuNP on top of the GNR. These findings are not only relevant for plasmonics, where the GNRs are commonly used as antennas for light, but may potentially be used in microfluidics as flow or electric field sensors (as outlined in the outlook section).

A few other applications of the assembly technique were trialled in collaborative work. Assembly of GNRs was achieved on a MMA coated substrate. The results were similar to the ones achieved on  $SiO_2/Si$  but had a significant advantage: they could easily be transferred to another substrate (as shown by Dr. C. Ng for  $TiO_2$ ). This greatly enhances the applicability of all shown assemblies and significantly reduces the time for parameter adjustments when changing the substrate material.

Other silicon chips with an etched channel structure were trialled for nanoparticle assembly as well. The assemblies successfully produced uniform core particle distributions and were further used to grow Si-nanowires. The resulting substrates could utilise the thermoelectric effect to produce electricity. The electrostatic assembly method here was particularly appealing, as the gold nanoparticles have uniform size and nearest neighbour distance.

Finally, electrostatic assembly was used to assemble polystyrene microspheres in a dense array on a  $TiO_2$  layer. The so produced arrays were used as a lithography mask to achieve perforated gold electrodes for back-contact perovskite solar cells.

### 7.3 Conclusion

In conclusion, all milestones set in the thesis objectives have been reached. The simple electrostatic assembly concept has proven to allow significant control over different, otherwise difficult to achieve, nanostructures. The method not only provides a facile large scale fabrication technique for sought after nanostructures, but has also been shown to be applicable to a variety of other fields. The research here presented is therefore expected to have impact in these fields and drive further innovations.

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## Appendix A

## **Computational Methods**

## A.1 Python Module: dlvolib.py

```
import numpy as np
import scipy.constants as constants
def Y_eff_s(T, Phi_0, I, a):
   Y_0 = (constants.e/(constants.k*T)) * Phi_0*0.001
   Phi_eff = ((constants.k*T)/constants.e) * ((8*np.tanh(
              (constants.e*Phi_0*0.001) / (4*constants.k*T))) /
              (1+(1-(((2*kappa(I, T)*a*10**(-9) + 1) /
                     (kappa(I, T)*a*10**(-9) + 1)**2) *
                     (np.tanh((constants.e*Phi_0*0.001) /
                              (4*constants.k*T)))**2))**0.5))
   Y_eff = constants.e/(constants.k*T) * Phi_eff
   return Y_eff
def Y_eff_p(T, Phi_0):
   Phi_eff = ((4*constants.k * T) / constants.e) * np.tanh(
              (constants.e*Phi_0*0.001) / (4*constants.k*T))
   Y_eff = constants.e/(constants.k*T) * Phi_eff
   return Y_eff
def kappa(I, T, epsilon_r=78.55):
   return np.float64(((2000*constants.N_A * (I*10**(-6)) *
                        (constants.e**2)) /
                       (constants.epsilon_0*epsilon_r*constants.k*T))**0.5)
def E_surface(z, T, ap, YS, YA, I, epsilon_r=78.55):
   static_prefactor = np.float64(4*constants.pi*constants.epsilon_0 *
```

```
epsilon_r * (constants.k/constants.e)**2)
    variable_prefactor = np.float64((T**2) * (ap*10**(-9)) * YS*YA)
    return (static_prefactor*variable_prefactor*np.float64(np.exp(
            np.float64(-kappa(I,T,epsilon_r)*(z*10**(-9)))))) / constants.e
def E_spheres(z, 1, T, ap, an, YN, YP, I, epsilon_r=78.55):
    ap *= 10**(-9)
    an *= 10 * * (-9)
    z = 10 + (-9)
    1 *= 10**(-9)
    static_prefactor = np.float64(4*constants.pi*constants.epsilon_0 *
                                  epsilon_r * (constants.k/constants.e)**2)
    variable_prefactor = np.float64((T**2) * (ap*an) * YN*YP)
    if (np.sqrt(1**2 + (z+ap-an)**2)) == 0.:
        return np.nan
    return (static_prefactor*variable_prefactor*np.float64(np.exp(
            (-kappa(I,T,epsilon_r) *
             ((np.sqrt(1**2 + (z+ap-an)**2)) - (ap+an))))) /
            (np.sqrt(l**2 + (z+ap-an)**2))) / constants.e
def E_VdW_s(z, 1, a1, a2, A_H=(2.5*10**(-19))):
    a1 *= 10**(-9)
    a2 *= 10 * * (-9)
    z *= 10**(-9)
    1 *= 10**(-9)
    i = (np.sqrt(l**2 + (z+a2-a1)**2)) - (a2+a1)
    \log = (2*(a2+a1)*i + i**2) / (4*a2*a1 + 2*(a2+a1)*i + i**2)
    if log <= 0.:
        return np.nan
    E = (-A_H/6) * (((2*a2*a1) / (2*(a2+a1)*i + i**2)) +
                    ((2*a2*a1) / (4*a2*a1 + 2*(a2+a1)*i + i**2)) +
                    np.log(log))
    return E/constants.e
def E_VdW_p(z, ap, A_Sub=(5.7*10**(-20))):
    ap *= 10**(-9)
    E = -((A_Sub/6) * ((ap/z) + (ap/(2*ap + z)) + np.log(z/(2*ap + z))))
    return E/constants.e
if __name__ == "__main__":
    print "Module only, no stand alone usage."
```
#### A.2 Plasmonics Calculations

This section contains code snippets for the different tasks of the BEM calculations.

Setting up the dielectric constants of the environment (epsb) and the nanoparticles (epsau):

```
epsb = epsconst(1.3<sup>2</sup>);
epsau = epstable('gold.dat');
epstab = {epsb, epsau};
```

Defining the geometry of a sphere with radius  $\mathbf{r}$ .  $\mathbf{n}$  is a scaling factor, which determines the number of nodes for the mesh grid of a particle.

```
n = 35
n = round(n * sqrt((r/15)));
t = linspace(0, 2*pi, n*0.75);
ao = log10(1e-3);
ae = log10(0.5*pi);
phi1 = logspace(ao, ae, n);
d_lin = phi1(end) - phi1(end-1);
n_equal = round(1.5/d_lin) + 1;
phi2_t = linspace(0, 0.5*pi, n_equal);
phi2 = fliplr(-phi2_t + pi);
phi = [phi1, phi2];
[phi, t] = meshgrid(phi, t);
x_0 = sin(phi).*cos(t);
y_0 = sin(phi).*sin(t);
z_0 = cos(phi);
x = r * x_0;
y = r*y_0;
z = r*z_0;
clear p
[faces, verts] = surf2patch( x, y, z, 'triangles');
p = clean(particle(verts, fliplr(faces)));
```

Different particles (p1, p2) can be combined to one assembly with specified dielectric properties:

p = comparticle(epstab, {p1, p2}, [2,1; 2,1], [1,2]);

Setting up the different BEM solvers:

```
%number of modes to use for the eigenmode solver
nev = 100;
bem_stat = bemstateig(p, 'nev', nev);
```

```
%options for retarded solver
op = bemoptions('sim', 'ret', 'interp', 'curv');
bem_ret = bemsolver(p, op);
```

Defining a plane wave excitation:

```
%for the eigenmode solver, specifying light polarisation
%(here: x-polaisaton)
exc_stat = planewavestat([1, 0, 0]);
```

%for the retarded solver, specifying light polarisation and %propagation direction (here: x-polaisaton and z-direction) exc\_ret = planewaveret([1, 0, 0], [0, 0, 1]);

Using the excitation to calculate the absorption cross section at the different wavelengths (here shown for the static case):

```
enei = 400:1:800; %wavelenght region to calculate
enei = enei(:);
sa = zeros(length(enei), 1);
%iterate the wavelenghts
for i=1:length(enei)
   sig_stat = bem_stat \ exc(p, enei(i));
   sa(i) = exc_stat.abs(sig_stat);
end
```

In order to calculate the E-field intensity map, the surface charge distribution for a given excitation is used (retarded case):

```
sig = bem_ret \ exc_ret(p, 610);
%define the grid step size for the map and initialise the map with zeros
steps = 0.1;
ry = -(2*r3)/2 : steps : (2*r3)/2;
rx = -(2*r1+r2+5) : steps : (2*r3+r2+5);
z = zeros(length(rx), length(ry));
%iterate over the grid points and calculate the |E|^2
for i=1:length(rx)
  for j=1:length(ry)
    R = [rx(i), ry(j), 0]; %vector pointing to the current grid position
    Rp = p.pos; %particle points/positions with known surface charge
    r = repmat(R, length(Rp), 1) - Rp; % R - Rp vector
    r_abs = sqrt(sum(r.^2, 2)); % |R - Rp|
    r_abs = r_abs.^3; %|R - Rp|^3
    % G = (R - Rp) / |R-Rp|^3
    G(:, 1) = r(:, 1). / r_abs;
    G(:, 2) = r(:, 2)./r_abs;
```

```
G(:, 3) = r(:, 3)./ r_abs;
s = sig.sig2; %surface charge dist due to excitation
% Electric field at R:
% E(R) = \sum_{Rp} sigma(Rp) G(R,Rp) Area(Rp)
aEf = sum(repmat(p.area, 1, 3).* (s.*G));
%put calculated |E|^2 into the map
z(i,j) = aEf*aEf';
end
end
```

For the case of an electron excitation, one needs to define additional parameters (after setting up the bem\_ret):

```
% electron velocity (energy: 80keV) and width (5 nm) of the electron beam
[vel, width] = deal(eelsbase.ene2vel(80e3), 5);
```

```
%the impact parameter (here: position (0, 0); can also be a mesh if a map
%shall be calculated):
imp = [0, 0];
```

The excitation is then initialised with:

```
exc = electronbeam(p, imp, width, vel, op, 'cutoff', 10);
```

Electron energy loss cross section and scattering cross section (cathodoluminescence) can than be obtained for a given wavelength (here: 600 nm):

```
%set up a sphere at infinity to determine the far field
spec = spectrumret;
sig = bem_ret \ exc(600);
%retrieve surface and bulk EEL
[psurf, pbulk] = exc.loss(sig);
%calculate far field and retrive the CL signal
[sca, ~] = scattering(farfield(spec, sig));
```

Appendix B

# Size Selective Adsorption of Gold Nanoparticles

B.1 Example SEM Image



Figure B.1: SEM image of a typical assembly for a 1:1 satellite solution after 3 h incubation at 20 °C. (Scale bar:  $1 \,\mu$ m)

### Appendix C

### **Plasmonic Trimer Nanolenses**

### C.1 Additional SEM Image of a Trimer Assembly



Figure C.1: An additional SEM image of sample with an optimised trimer assembly. The green circles indicate the trimers with a bending angle smaller  $55^{\circ}$  and thus regarded as rather linear. (Scale bar: 500 nm)

### Appendix D

## Towards Other Particle Materials and Shapes

D.1 SEM Image of AgNPs on a  $SiO_2$  substrate



Figure D.1: SEM image of TMAC functionalised AgNPs on a bare  $SiO_2$  substrate. Small fragments are visible around the AgNPs. (Scale bar: 250 nm)

D.2 Overview SEM Image of a GNR Assembly with 30 nm Core Particles



Figure D.2: SEM image of TMAC functionalised GNRs assembled on 30 nm AuNP cores. (Scale bar: 250 nm)

### Appendix E

### **Publications and Presentations**

#### E.1 Publications Related to the Thesis Topic

Size Selective Adsorption of Gold Nanoparticles by Electrostatic Assembly Julian A. Lloyd, Soon Hock Ng, Timothy J. Davis, Daniel E. Gómez and Udo Bach J. Phys. Chem. C, 2017, 121 (4), 2437-2443

Plasmonic Nanolenses: Electrostatic Self-Assembly of Hierarchical Nanoparticle Trimers and Their Response to Optical and Electron Beam Stimuli Julian A. Lloyd, Soon Hock Ng, Amelia C. Y. Liu, Ye Zhu, Wei Chao, Toon Coenen, Joanne Etheridge, Daniel E. Gómez and Udo Bach ACS Nano, 2017, 11 (2), 1604–1612

#### E.2 Presentations

A Simple Electrostatic Assembly Process for Gold Nanolens Arrays (poster) Nanotechnology Entrepreneurship Workshop for Early Career Researchers; Gold Coast, Australia, 2015

Electrostatically Assembled Gold nanolens Arrays for Enhanced Nearfield Focusing (talk) SPIE Micro+Nano Materials, Devices, and Applications; Sydney, Australia, 2015

Size-Selective Adsorption of Gold Nanoparticles on a Self-Assembled Template (poster)

International Conference on Nanoscience and Nanotechnology; Canberra, Australia, 2016

### Electrostatic Self-Assembly of Hierarchical Nanoparticle Trimers and their Response to Optical and Electron Beam Stimuli (talk)

European Materials Research Society Spring Meeting; Strasbourg, France, 2017

#### E.3 Publications Not Related to the Thesis Topic

### Dual-Function Smart Electrolyte for Dye-Sensitized Solar Cells: 5-Mercaptotetrazoles as Redox Mediator and Corrosion Repressor

Rishabh Bhargava, Torben Daeneke, Simon J. Thompson, Julian A. Lloyd, Carlos-Andres Palma, Joachim Reichert, Johnnes V. Barth, Leone Spiccia and Udo Bach J. Phys. Chem. C, **2015**, 119 (34), 19613–19618

## Surface-Assisted Cyclodehydrogenation; Break the Symmetry, Enhance the Selectivity

Alissa Wiengarten, Julian A. Lloyd, Knud Seufert, Joachim Reichert, Willi Auwärter, Runyuan Han, David A. Duncan, Francesco Allegretti, Sybille Fischer, Seung Cheol Oh, Özge Sağlam, Li Jiang, Saranyan Vijayaraghavan, David Écija, Anthoula C. Papageorgiou, and Johannes V. Barth

Chem. Eur. J., 2015, 21, 12285-12290

### Dynamics of Spatially Confined Bisphenol A Trimers in a Unimolecular Network on Ag(111)

Julian A. Lloyd, Anthoula C. Papageorgiou, Sybille Fischer, Seung Cheol Oh, Özge Sağlam, Katharina Diller, David A. Duncan, Francesco Allegretti, Florian Klappenberger, Martin Stöhr, Reinhard J. Maurer, Karsten Reuter, Joachim Reichert, and Johannes V. Barth Nano Lett., **2016**, 16 (3), 1884–1889