

Electromagnetic Coupling Phenomena in Self-Assembled Plasmonic Superstructures

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Abstract

This thesis contributes to the field of nanoparticle self-assembly and the investigation of optically active plasmonic surfaces. For the first time, it describes the systematic development of self-assembled, square centimeter sized nanoparticle arrays with tunable surface lattice resonances (SLRs). SLRs are strong collective plasmonic modes, which are formed due to coupling between the single particle plasmonic mode and the diffractive mode of the lattice. Due to their adjustable optical properties and responsiveness towards their environment, SLRs are subject of research for the development of e.g sensoric and optical applications.

The first chapter focuses on the preparation of wet-chemically synthesized gold/silver-poly-*N*-isopropylacrylamide (Au/Ag-PNIPAM) core-shell nanoparticles and their self-assembly into macroscopic, hexagonally ordered particle arrays. First, the synthesis of Au-PNIPAM and Ag-PNIPAM particles with core sizes ranging from 20 nm to 100 nm obtained by overgrowth of Au-PNIPAM seed particles is introduced. These particles are subsequently used to form the ordered particle monolayers at an air/water interface, which are then transferred onto glass substrates. The soft, deformable and thermoresponsive PNIPAM hydrogel shell provides colloidal stability and dictates the assembly at the interface. Since the same seed particles were used for each synthesis, the hexagonally ordered monolayers possess similar center-to-center distances (d_{c-c}), independent of their core size. This allows the tuning of the localized surface plasmon resonance (LSPR) of the particle array by varying only the plasmonic core size or material.

Based on this, next chapter focuses on the assembly process and monolayer extension behavior at the air/water interface originating from the deformable hydrogel shell. A time-dependent, collective monolayer expansion is observed at the interface as the particle shells stretch out at the interface in order to reduce the interfacial pressure. Consequently, by repeated extraction of macroscopic particle monolayers from only one large floating monolayer, particle monolayers with steadily increasing d_{c-c} can be obtained. Using atomic force microscopy the order and dimensions of the lattices are investigated and UV-vis absorbance spectroscopy is used to relate the d_{c-c} to the plasmonic properties of the arrays. For small center-to-center distances, a collective interaction of the particles within the lattice is found. This long range dipole coupling leads to an increased quality factor ($Q = \text{Peak maximum wavelength } \lambda / \text{Full-width at Half-Maximum FWHM}$) of the resonance.

The third paper addresses self-assembled plasmonic silver nanoparticle monolayers that exhibit surface lattice resonances (SLRs). This goal is achieved by homogenization of the refractive index environment of the particle array with a polymer coating. Like this, the LSPR of the single particles can couple with an in-plane diffractive mode of the lattice (Bragg mode), given that a sufficiently large overlap between these two modes is ensured. In comparison to a single particle LSPR ($Q_{\text{single LSPR}} \approx 3-4$) or the weakly coupled array in the uncoated case ($Q_{\text{LSPR}} \approx 8-9$), the Q-factor further increases ($Q_{\text{SLR}} \approx 14$). Additionally, a shift of the resonance towards higher wavelengths is found upon an increase of either the refractive index or the d.c.-c. By employing the temperature sensitive polymer PNIPAM as top-coating a fully reversible tunability of the SLR in water is demonstrated.

Next, the spectral properties dependent on the coating thickness are studied. Silver and gold nanoparticle arrays are employed and coated with an increasingly thick polymer coating (up to 2 μm). By doing so, higher-order, thickness-dependent resonances are identified within the LSPR -region. Furthermore, it is found that less than 500 nm top-coatings are enough to achieve a fully developed SLR. Based upon this, free-standing plasmonic films below 1 μm in total thickness are prepared, which possess strong SLRs.

The last two studies extend the nanostructures obtainable using self-assembly at the air/water interface to Moiré and honeycomb lattices. For this, a double deposition process is developed and the structure formation is investigated using Brownian dynamics simulations. It is found that fast drying of the second deposited monolayer freezes the structure in place and leads to the formation of Moiré structures. Slow drying, on the other hand, gives the system the chance to equilibrate and find an energy minimum, which results in a honeycomb structure. Both, Moiré and honeycomb lattices, show SLRs in a wavelength range comparable to the hexagonally ordered samples of the same particle type and diffraction wavelength. The reduced domain sizes, originating from the double deposition process, result in less pronounced SLR features. However, the fact that the SLR can still be measured in samples with domain sizes with less than 100 particles proves the robustness of SLR modes with respect to disorder.

Altogether, this thesis gives design rules for the fabrication of plasmonic surfaces and the tailoring of SLRs in self-assembled particles arrays. This represents a promising starting point for the extension to other particle systems and testing in functional devices.

Zusammenfassung

In dieser Arbeit werden Beiträge zu dem Forschungsfeld der Selbstanordnung von Nanopartikeln und der Erforschung von optisch aktiven, plasmonischen Oberflächen beschrieben. Dabei wird die systematische Entwicklung von selbst-assemblierten, quadratzentimeter-großen Nanopartikelanordnungen mit einstellbaren Oberflächengitterresonanzen (engl. Surface Lattice Resonance SLR) sowie deren Charakterisierung behandelt. SLRs sind starke kollektive, plasmonische Moden, die durch Kopplung zwischen der Oberflächenplasmonenresonanz (LSPR) der Einzelpartikel und der Bragg Mode des Partikelgitters gebildet wird. Aufgrund ihrer einstellbaren optischen Eigenschaften und ihrer Abhängigkeit von ihrer Umgebung, sind SLRs Ziel der Forschung für die Entwicklung von beispielsweise Sensorik- oder Optikanwendungen.

Im ersten Kapitel liegt der Fokus auf der nasschemischen Herstellung von Gold/Silber-Poly-*N*-Isopropylacrylamid (Au/Ag-PNIPAM) Kern-Schale Nanopartikeln und deren Selbstanordnung zu makroskopischen, hexagonal angeordneten Partikelgittern. Zunächst wird die Synthese von Au-PNIPAM und Ag PNIPAM Partikeln mit Kerngrößen von 20 nm bis 100 nm vorgestellt. Hierbei werden die ursprünglichen Au-PNIPAM Keimpartikeln mit Gold oder Silber überwachsen. Die Partikel werden anschließend genutzt, um geordnete Partikelmonolagen an der Luft/Wasser-Grenzfläche zu bilden, welche anschließend auf Glassubstrate übertragen werden. Die weiche, verformbare und temperaturresponsive Hydrogelschale der Keimpartikel verleiht dem Partikel kolloidale Stabilität und bestimmt das Anordnungsverhalten an der Grenzfläche. Da die gleichen Keimpartikel für alle Synthesen verwendet werden, besitzen alle hergestellten hexagonal-geordneten Partikelmonolagen einen ähnlichen Zentrum-zu-Zentrum Abstand (d_{c-c}) - unabhängig von ihrer Kerngröße. Dies ermöglicht die gezielte Untersuchung des Einflusses der Kern-Parameter (Material oder Größe) auf die lokalisierte Oberflächenplasmonenresonanz (LSPR) des Partikelgitters.

Das nächste Kapitel konzentriert sich auf den Assemblierungsprozess und das Ausbreitungsverhalten der Monolage an der Luft/Wasser Grenzfläche, welches durch die verformbare Hydrogel-Hülle der Partikel bestimmt werden. An der Grenzfläche kann eine zeitabhängige, kollektive Ausbreitung der Monolage beobachtet werden. Die ist das Resultat der sich ausdehnenden Partikelschalen an der Grenzfläche, wodurch die Grenzflächenspannung der Luft/Wasser-Grenzfläche reduziert wird. Daher ist es möglich, durch wiederholte Entnahme von makroskopischen Partikelmonolagen aus einer einzigen schwimmenden Partikelmonolage, mehrere Partikelmonolagen mit stetig steigenden d_{c-c} -Werten herzustellen. Mittels

Rasterkraftmikroskopie und UV-vis Spektroskopie werden die plasmonischen Eigenschaften der 2D-Gitter mit den Gitterparametern korreliert. Für geringe Zentrum-zu-Zentrum Abständen wird eine kollektive Wechselwirkung der plasmonischen Partikel im Gitter beobachtet. Diese weitreichende Dipol-Dipol-Kopplung führt zu hohen Qualitätsfaktoren (Q) der Resonanzen.

Die dritte Publikation beschäftigt sich mit selbst-angeordneten plasmonischen Silbernanopartikel-Monolagen, welche Oberflächengitterresonanzen (LSRs) zeigen. Dieses Ziel wird erreicht, indem die Brechungsindexumgebung des Partikel-Gitters durch eine Polymerbeschichtung homogenisiert wird. Hierdurch kann die LSPR der Einzelpartikel mit in der Ebene liegenden Bragg Moden des Gitters koppeln. Dies gelingt nur, wenn ein ausreichend großer Überlapp der beiden Moden sichergestellt werden kann. Im Vergleich zur Einzelpartikel LSPR ($Q_{\text{Einzel LSPR}} \approx 3-4$) oder dem schwach-koppelnden Partikelgitter im nicht-beschichteten Fall ($Q_{\text{LSPR}} \approx 8-9$) nimmt der Q -Faktor weiter zu ($Q_{\text{SLR}} \approx 14$). Zusätzlich wird eine Verschiebung der Resonanz zu höheren Wellenlängen beobachtet, wenn entweder der Brechungsindex oder d_{c-c} erhöht wird. Des Weiteren wird durch die Verwendung des temperatur-sensitiven Polymers PNIPAM als Beschichtung eine komplett reversibel einstellbare SLR in Wasser demonstriert.

Als nächstes werden die spektroskopischen Eigenschaften der hexagonalen Partikelgitter in Abhängigkeit von der Schichtdicke der Beschichtung untersucht. Silber- und Goldnanopartikel-Gitter werden genutzt und mit einer zunehmend dicken Polymerschicht beschichtet (bis zu 2 μm). Dadurch werden höhergradige, schichtdickenabhängige Resonanzen innerhalb der LSPR-Region identifiziert. Weiterhin wird gezeigt, dass eine Beschichtung von weniger als 500 nm Dicke ausreicht, um eine vollständig ausgebildete SLR zu erzeugen. Basierend auf diesem Fund, wird ein freistehender plasmonischer Film, mit einer Gesamtdicke von weniger als 1 μm hergestellt, der eine stark ausgeprägte SLR zeigt.

Die letzten beiden Studien erweitern die herstellbaren Nanostrukturen durch Selbstanordnung an einer Grenzfläche auf Moiré und Honigwaben-Strukturen. Hierfür wird ein doppelter Abscheidungsprozess entwickelt und die Strukturbildung wird mittels Brown'scher Dynamiksimulationen erklärt. Es wird demonstriert, dass ein schnelles Eintrocknen der zweiten Monolage auf der Ersten zu einem sofortigen Einfrieren der Struktur führt und dadurch Moiré-Strukturen entstehen. Langsames Eintrocknen hingegen lässt dem System die Möglichkeit ein energetisches Minimum zu erreichen, was zur Bildung von Honigwaben-Strukturen führt. Bei beiden Strukturen, Moiré- und Honigwaben-Gitter, können SLRs gemessen werden. Diese liegen in dem gleichen Wellenlängenbereich wie die der hexagonal geordneten Proben mit

gleichen Partikeltyp und Beugungswellenlänge. Die reduzierte Domänengröße, die durch den Doppelabscheidungsprozess verursacht wird, resultiert in weniger deutlich ausgebildeten SLRs. Jedoch zeigt die Tatsache, dass selbst in Proben mit Domänengrößen von weniger als 100 Partikeln noch SLRs gemessen werden können, wie robust diese Moden gegenüber Unordnung sind.

Zusammenfassend bietet diese Arbeit einen Werkzeugkasten für das Design plasmonischer Oberflächen sowie das Einstellen von SLRs in selbst-angeordneten Partikelmonolagen. Dies ist ein vielversprechender Ausgangspunkt für den Übertrag auf andere Partikelsysteme und den Einsatz plasmonischer Partikelmonolagen in photonischen Anwendungen.

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1 Introduction

Many marvelous phenomena found in nature like vivid colors, extraordinary tough or stable materials, self-cleaning effects and the reversible adhesion of Gecko feet can all be traced back to one common origin: structural order and hierarchical design. The origin of structural colors, for example, can be subdivided into thin-film¹⁻³ and multi-film⁴⁻⁸ reflections, diffraction gratings⁹⁻¹³, scattering¹⁴ and photonic crystals in two¹⁵⁻¹⁷ or three¹⁸⁻²⁰ dimensions.²¹⁻²² Thin film and multi-film effects lead to the iridescent colors of fish^{6, 23-25} and butterflies²⁶⁻²⁹. The latter additionally show colors due to a 3D photonic crystal structure of the wings made of porous chitin structures.^{18, 30-31} Likewise, periodic arrays of solid rods are the reason for the brilliant iridescent colors of the male peacock's tail feathers.³²⁻³³ True to the maxim by Albert Einstein: "Look deep into nature, and then you will understand everything better", scientists up to date try to imitate nature in order make use of these effects also in artificial materials. The possibility to manipulate light with structures on the nanometer scale promises huge advances on various fields such as data storage or sensing. The structures in nature that enable the formation of structural effects usually possess the dimensions of a few nano- to micrometers and thus the terms of nanostructures, nanoparticles and colloids were shaped. The word nano originates from the old greek word νᾶνος (nános- dwarf)) and describes a size-range between 1 to 100 nm. By this strict definition, a nanostructured surface for example consists only of nanometer-sized features and nanoparticles possess dimensions below 100 nm. In order to classify also slightly larger particles, the term colloid is typically used. Colloidal particles are particles dispersed in a medium, where at least one spatial dimension is on the length scale between 1 nm and 1 μm ³⁴ and thus includes nanoparticles in their definition.

Creating such nanostructures from materials with a high density of free electrons and resonance frequency in the wavelength range of visible light opens up an entirely new world of optical phenomena that are not found in nature. Metal nanoparticle solutions of gold and silver for example also possess vivid colors but their origin is based on a different physical concept. Here excitations of the free electrons on a nanoparticles surface lead to the absorption and scattering of a certain wavelength of visible light and therefore to size and shape dependent colors.³⁵⁻³⁶ These resonances are called localized surface plasmon resonances (LSPRs). This beautiful effect, although not knowing the physics behind it, has already been used by the Romans to color glass³⁷⁻³⁸. When such metallic nanoparticles are arranged into periodic arrays, coupling between photonic modes of the crystal and plasmonic modes of the metal nanoparticles can take place.³⁹ Like this the relatively high damping losses inherent to single silver or gold

nanoparticles can be overcome.⁴⁰ The LSPRs with short lifetimes and low quality factors can be turned into strong plasmonic-photonic coupled modes called surface lattice resonances (SLRs) with significantly reduced absorption losses and high quality factors.³⁹ To enable this coupling the diffractive mode of the lattice needs to be in the wavelength-range of the LSPR.³⁹ Single particle properties like particle size³⁵⁻³⁶, shape⁴¹⁻⁴² and polydispersity⁴³ as well as lattice properties like lattice spacing⁴⁴⁻⁴⁵, size⁴⁶⁻⁴⁷, geometry⁴⁷ and order⁴³ as well as global factors like refractive index environment⁴⁴ can be used to manipulate and optimize the resonance quality and wavelength position.

This coupling phenomenon and first applications thereof, like dye coupling for plasmonic nanolasers⁴⁸⁻⁵¹, SERS⁵² and refractive index sensors⁵³ as well as coupling to electronic materials⁵⁴⁻⁵⁶, LEDs⁵⁷⁻⁶⁰, solid-state lighting⁶¹⁻⁶³, were demonstrated during the last years in and with lithographically produced samples. Design rules and possible modifications were studied in great detail and multiple theoretical approaches were used to predict and confirm the optical response of such systems.^{39, 43-45, 47, 64-66}

However, the fabrication of structures on this small scale remains challenging. A high precision is needed regarding the size, shape and uniformity of the building blocks as well as the degree of order and uniformity of the formed superstructures. In general, nanostructures can be produced using top-down or bottom-up approaches. Top-down or direct-write approaches start from a macroscopic material that is broken down to the desired size and structure. The typically employed direct-write methods on lab scale like electron-beam lithography and focused ion-beam etching are advantageous to prepare arbitrarily shaped nanostructures, but scaling array areas is difficult and the overall production costs are the main limitations for new applications.⁶⁷ Conventional photolithography is restricted to feature sizes of approximately the double wavelength by the diffraction limit. Lately, large throughput processes based on extreme ultraviolet light (EUV) photolithography, which can reach feature sizes of < 20 nm, have been introduced into mass production.⁶⁸⁻⁶⁹ New nanofabrication methods using poly(dimethylsiloxane) (PDMS) stamps⁷⁰ like PEEL^{50, 71-73} (Photolithography + E-beam deposition + Etching + Lift-off) and SCIL⁶⁰ (Surface Conformal Imprint Lithography) give the opportunity to generate large area arrays, but are still very complex. This thesis is dedicated to the optimization of the much cheaper and more versatile bottom-up technique using chemical synthesis and self-assembly. It will be shown that high quality macroscopic nanoparticle arrays, which show coupling between plasmonic and photonic modes can be produced by self-assembly at the air/water interface and subsequent transfer to a solid support. Furthermore, the tunability of the optical modes using particles of different materials, variation in lattice spacing

and lattice geometries as well as the refractive index environments will be demonstrated for the first time in self-assembled nanostructures.

In this thesis, I will first introduce optical properties of single metal nanoparticles and 2D arrays as well as the current state of the art (Chapter 1.1). Then, I will give an overview over colloidal particles as well as synthesis routes of metal nanoparticles and core/shell particles in Chapter 1.2. After that, different routes for nanoparticle assembly and the competing forces acting at the air/water interface will be presented (Chapter 1.3). In the second section, I will give short summaries of every publication used in this cumulative thesis (Chapter 2.2) and give account of my personal contributions to the publications (Chapter 2.3). In sections 3 – 8 the full publications can be found. Finally, Chapter 9 discusses possible implications of this work and presents an outlook on future challenges and possibilities regarding self-assembled, plasmonic surfaces.

1.1 Light-Matter Interactions in Plasmonic 2D Nanoparticle Arrays

Plasmons are collective oscillations of electrons in a solid excited by an incoming electromagnetic wave. Depending on the dimensions of the solid, three types of plasmons can be distinguished: (1) Volume plasmons, which occur due to longitudinal electron density oscillations in bulk materials, (2) Surface plasmon polaritons (SPP) - two dimensional, transverse oscillations of electrons bound to a metal/dielectric interface, and finally, (3) localized surface plasmons (LSP), which are in-phase oscillations of electrons in deep-subwavelength scale particles. As a high density of free electrons is a prerequisite for the occurrence of these phenomena, plasmons are mainly found in metals.

In order to understand the origin of plasmons, one needs to have a look at the interaction of matter, in our case metals, with light. Light can be described as an electromagnetic wave and the interaction of its electric field with the atoms of a material (here metals) can be analyzed based on the Drude model. As we know from everyday experience, metals are usually highly reflective for frequencies up to the frequency range of visible light and are electrically conductive. This means that electromagnetic waves cannot penetrate through them, making them the ideal material for waveguides and resonators for applications in microwave and infrared-frequencies. When higher frequencies in the near-infrared and visible region are considered, the field can penetrate significantly into the metal and its performance in photonic devices for example as waveguide diminishes due to an increase in loss. Finally, in the ultraviolet region, metals behave like dielectrics and allow the propagation of electromagnetic waves, i.e. they become transparent and for example X-rays can pass through them. This transparency might be reduced due to the exact band structure of the metal, as the transitions between electronic bands in gold and silver for example lead to additional loss channels (absorption). The overall frequency-dependent (dispersive) behavior can be described by a complex dielectric function $\epsilon(\omega)$.³⁶ The Lorentz model³⁵ can describe the response of an isotropic, dielectric medium to an external electromagnetic wave. In this model, a mass m is bound to a spring with a natural frequency ω_0 , with m being the mass of an electron. Attached to the mass is a damper with a certain damping (frictional) factor γ . The application of a time-dependent electric field $\vec{E}(t)$ leads to a displacement x of the mass by pulling on the spring.

$$\text{Lorentz equation of motion} \quad \underbrace{-e\vec{E}(t)}_{\text{driving (electric) force}} = \underbrace{m\ddot{x}}_{\text{acceleration force}} + \underbrace{m\gamma\dot{x}}_{\text{frictional force}} + \underbrace{m\omega_0^2 x}_{\text{restoring force}} \quad (1.1)$$

For metals, the Drude model, a special case of the Lorentz model, is applicable. Here, the restoring force, originating from the closely bound electrons in dielectrics and their natural

frequency, is neglected because the electrons in metals are assumed to be freely floating in an “electron cloud” as described in the plasma model. Therefore, the following picture applies.

When an electromagnetic wave hits the metal, the charge distribution in the metal, which is composed of a lattice of large, immobile, positively charged nuclei and small, delocalized, negatively charged electrons, is disturbed. The electrons, in the freely floating electron gas oscillate in response to the electric field $\vec{E}$. Collisions with the nuclei, caused by the random motion of the electrons based on the kinetic gas theory, cause a damping of these oscillation with the damping frequency $\gamma = \frac{1}{\tau}$ with τ being the average time between collisions.³⁶ These assumptions can be summarized into a time-dependent equation of motion of an electron in the electron gas:³⁶

$$\text{Drude equation of motion: } -e\vec{E}(t) = m\ddot{\vec{x}} + m\gamma\dot{\vec{x}} \quad (1.2)$$

With e and m being the charge and the mass of an electron. Applying a harmonic oscillation as electric field³⁶

$$\vec{E}(t) = \vec{E}_0 \cdot e^{-i\omega t} \quad (1.3)$$

with the amplitude $\vec{E}_0$ and the angular frequency ω yields the following expression for the displacement:³⁶

$$\vec{x}(t) = \vec{x}_0 \cdot e^{-i\omega t} = \frac{e}{m(\omega^2 + i\gamma\omega)} \vec{E}(t) \quad (1.4)$$

The macroscopic property connected to the displacement of the electrons in an isotropic medium is called polarization $\vec{P}$ and is given by

$$\vec{P} = -ne\vec{x}(t) = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)} \vec{E}(t) = (\epsilon_r - 1)\epsilon_0 \vec{E}(t) \quad (1.5)$$

with the number density of charge carriers n , the vacuum permittivity ϵ_0 and the relative permittivity in the medium ϵ_r . This yields the dielectric function of metals with the plasma frequency ω_p :⁷⁴

$$\epsilon_r = 1 - \frac{ne^2}{\epsilon_0 m(\omega^2 + i\gamma\omega)} = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} \quad (1.6)$$

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \quad (1.7)$$

The dielectric function can be separated into a real ϵ'_r and an imaginary part ϵ''_r :

$$\varepsilon_r(\omega) = \varepsilon'_r(\omega) + i\varepsilon''_r(\omega) \quad (1.8)$$

$$\varepsilon'_r = 1 - \frac{\omega_p^2 \tau^2}{(1 + \omega^2 \tau^2)} \quad (1.9)$$

$$\varepsilon''_r = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} \quad (1.10)$$

In Figure 1.1, the wavelength (a) and frequency (b) dependent real and imaginary parts of the dielectric function of gold are shown. The values for the plasma frequency $\omega_p = 13.8 \cdot 10^{15} \frac{1}{s}$ and for the loss frequency $\gamma = \frac{1}{\tau} = 1.1 \cdot 10^{14} \frac{1}{s}$ were taken from literature.⁷⁴

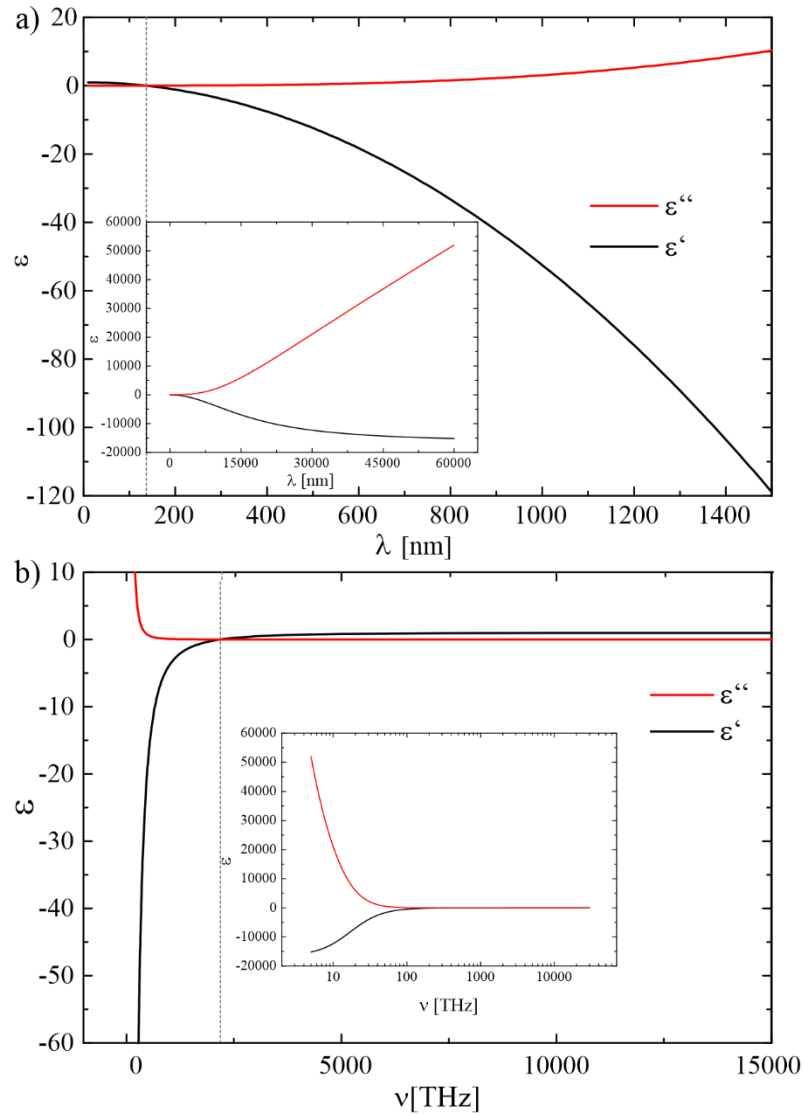


Figure 1.1 Drude response of gold in dependence of (a) the wavelength and (b) the frequency.

Both depictions display the same information however, as a chemist the wavelength-dependent plot appears more familiar whereas most discussions in literature are done in terms of frequency. The plasma wavelength/frequency (gray dashed lines) is the eigenfrequency of the

bulk plasmon and occurs due to the collective, longitudinal oscillation of the electron gas around the fixed nuclei in the metal. Below that frequency the real part of the dielectric function (black line) becomes negative and the imaginary part reaches very high values. This is the reason for the high reflectivity of metals in response to an external electric field at low frequencies and the wave cannot penetrate into the metal. Above the plasma frequency, on the other hand, the real part of the metal is positive and the oscillations of an incoming electromagnetic wave are too fast for the electrons to follow. At the same time the imaginary part approaches zero, indicating vanishing losses. Therefore, metals become transparent at high frequencies. The plasma frequency of metals like Ag (137.62 nm, 2180 THz) and Au (137.31 nm, 2185 THz) lies in the UV and therefore metals become lossy at optical frequencies. An additional effect, which is neglected in the Drude model is the occurrence of interband transitions in the UV region, which cause additional losses (damping).³⁶ This damping can be accounted for by the introduction of the classical picture from the Lorentz model of a bound electron with a resonance frequency ω_0

$$-e\vec{E}(t) = m\ddot{x} + m\gamma\dot{x} + m\omega_0^2x \quad (1.11)$$

which results in the dielectric function ε_L for the Lorentz damping of⁷⁴

$$\varepsilon_L = 1 + \frac{\omega_1^2}{(\omega_0^2 - \omega^2 - i\gamma_1\omega)} \quad (1.12)$$

where ω_1 and γ_1 are related to the corresponding frequency and damping of the bound electron, respectively. Combining the result from the Drude model with the result for the Lorentz oscillator the modified dielectric constant ε_{DL} is obtained:⁷⁵

$$\varepsilon_{DL} = 1 - \frac{\omega_p^2}{(\omega^2 + i\gamma\omega)} + \sum_{j=1}^K \frac{f_j\omega_j^2}{(\omega_j^2 - \omega^2 - i\gamma_j\omega)} \quad (1.13)$$

In this expression multiple interband transitions K can be taken into account with the resonant frequency ω_j , the weighting coefficient f_j and the damping frequency γ_j . Like this the theoretical data of the Drude(-Lorentz) model can be fitted to experimentally determined values as depicted in Figure 1.2. The calculated data using the Drude model (dashed line) fits the experimental data for the dielectric function of gold (solid line) well down to approximately 600 nm. At lower wavelengths, the deviation caused by interband transitions are nicely overcome by the application of the Drude-Lorentz (DL) model (bold solid line).⁷⁶

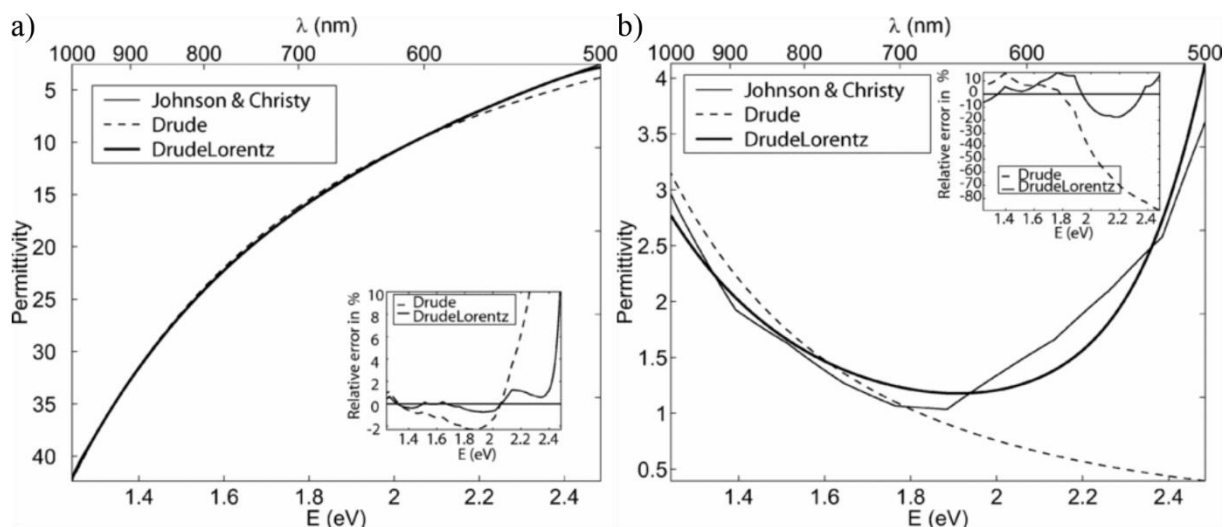


Figure 1.2 Comparison of real (a) and imaginary (b) part of the permittivity (= dielectric function) from experimental data provided by Johnson and Christy⁷⁷ (solid line), the Drude model (dashed line) and the Drude-Lorentz model (bold solid line). (a,b) Reprinted with permission from Ref. ⁷⁶. ©2005, American Physical Society.

Typically, this model is used in time-domain based numerical solvers for the Maxwell's equations, like the finite-difference time-domain (FDTD) scheme also employed in this thesis.^{76, 78}

1.1.1 Localized Surface Plasmon Resonances

Localized surface plasmons (LSP) are based on the non-propagating excitation of the conduction electrons of plasmonic nanostructures coupled to an electromagnetic field. For the simple case of spherical particles, the curved surface exerts an effective restoring force on the driven electrons, which enables the formation of resonances. Consequently, a field amplification can be observed inside and outside of the particle in the near-field zone. Furthermore, in contrast to propagating surface plasmon polaritons, which can only be excited with the help of phase matching techniques like a prism or lattice coupling, localized surface plasmons can be excited by direct illumination with light due to the curved surface.

As long as the size of a particle is much smaller than the wavelength of light in the surrounding medium the interaction of the particle with an electromagnetic field can be described by a simple, quasi-static approximation (Rayleigh approximation). One assumes that the phase of the harmonically oscillating electromagnetic field is constant over the entire particle volume. This approximation allows for an adequate description of the optical response of nanoparticles with dimensions below 100 nm. First, let us consider a homogenous spherical particle with the radius a and a frequency-dependent relative permittivity $\epsilon_r(\omega)$ in an isotropic, non-absorbing

medium with a dielectric function ϵ_m (which, in this context, will be regarded as frequency-independent) and a uniform electric field $\vec{E}_0$.

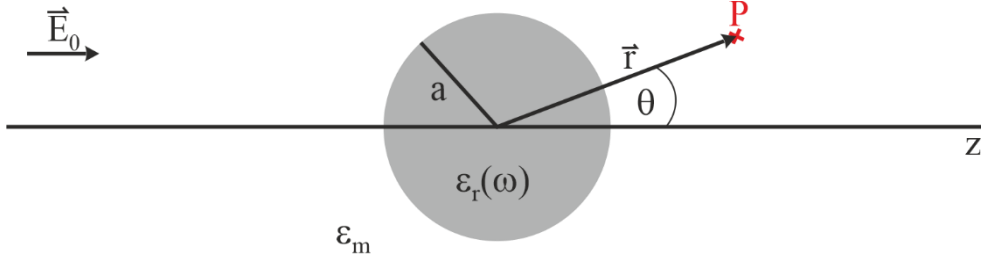


Figure 1.3 Sketch of a spherical particle in a isotropic, non-absorbing medium and a uniform electric field $\vec{E}_0$.

When the particle is excited, charge separation takes place and potentials inside and outside the particles occur:³⁶

$$\Phi_{in}(r, \theta) = -\frac{3\epsilon_m}{\epsilon_r(\omega) + 2\epsilon_m} E_0 r \cos\theta \quad (1.14)$$

$$\Phi_{out}(r, \theta) = \underbrace{-E_0 r \cos\theta}_{\text{applied field}} + \underbrace{\frac{\epsilon_r(\omega) - \epsilon_m}{\epsilon_r(\omega) + 2\epsilon_m} E_0 a^3 \frac{\cos\theta}{r^2}}_{\text{induced dipole field}} \quad (1.15)$$

With the position vector $\vec{r}$ and the angle θ between the z plane and P, a certain point in space, where the response is monitored. The potential outside the particle Φ_{out} can be rewritten with $\vec{p}$ as induced dipole moment:

$$\Phi_{out}(r, \theta) = -E_0 r \cos\theta + \frac{\vec{p} \cdot \vec{r}}{4\pi\epsilon_0\epsilon_m r^3} \quad (1.16)$$

$$\vec{p} = \epsilon_0\epsilon_m\alpha\vec{E}_0 \quad (1.17)$$

Where α is the complex polarizability of a small metal sphere with:

$$\alpha = 4\pi a^3 \frac{\epsilon_r(\omega) - \epsilon_m}{\epsilon_r(\omega) + 2\epsilon_m} \quad (1.18)$$

We see that a large polarizability leads to a strong resonance enhancement and that this achieved when $|\epsilon_r(\omega) + 2\epsilon_m|$ is at a minimum. When metals with a little-varying imaginary part are considered this simplifies to the Fröhlich condition:

$$\epsilon_r'(\omega) = -2\epsilon_m \quad (1.19)$$

For a sphere consisting of a Drude metal placed in air ($\epsilon_m = 1$) this criterion is fulfilled at a frequency of $\omega_0 = \frac{\omega_p}{\sqrt{3}}$ and results in a dipolar localized surface plasmon resonance. It is obvious

that the resonance position is highly dependent on the dielectric environment and a red-shift of the resonance is observed when ε_m is increased.

Since $\vec{E} = -\nabla\Phi$, the distribution of the electric field can be deduced from the potentials as the following:

$$\vec{E}_{in} = \frac{3\varepsilon_m}{\varepsilon_r(\omega) + 2\varepsilon_m} \vec{E}_0 \quad (1.20)$$

$$\vec{E}_{out} = \vec{E}_0 + \frac{3\vec{n}(\vec{n} \cdot \vec{p}) - \vec{p}}{4\pi\varepsilon_0\varepsilon_m} \frac{1}{r^3} \quad (1.21)$$

$\vec{n}$ equals a unit vector in the direction of the point of interest. Under plane wave illumination with $\vec{E}(\vec{r}, t) = \vec{E}_0 e^{-i\omega t}$, an oscillating dipole moment is induced:

$$\vec{p}(t) = \varepsilon_0\varepsilon_m\alpha\vec{E}_0 e^{-i\omega t} \quad (1.22)$$

The radiation of this dipole leads to scattering of the plane wave by the sphere, which can be represented by a radiating point dipole

As a consequence of the resonantly enhanced polarization α the metal nanoparticle will also scatter and absorb light more efficiently. For metallic Ag and Au spheres, these resonances occur in the visible wavelength range. This is the reason for the bright colors these particles exhibit in transmission and reflection caused by enhanced absorption and scattering. The scattering cross-section σ_{scat} and absorption cross-section σ_{abs} can be calculated using the following equations:³⁵⁻³⁶

$$\sigma_{scat} = \frac{k_0^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k_0^4 a^6 \left| \frac{\varepsilon_r(\omega) - \varepsilon_m}{\varepsilon_r(\omega) + 2\varepsilon_m} \right|^2 \quad (1.23)$$

$$\sigma_{abs} = k_0 \text{Im}(\alpha) = 4\pi k_0 a^3 \text{Im} \left(\frac{\varepsilon_r(\omega) - \varepsilon_m}{\varepsilon_r(\omega) + 2\varepsilon_m} \right) \quad (1.24)$$

Where k_0 is the wave vector defined by $k_0 = \frac{2\pi}{\lambda}$. Consequently, the scattering cross-section as well as the absorption cross-section scale strongly with the nanoparticle size. Due to the a^6 dependence of scattering and the a^3 dependence of absorption, absorption will dominate for small particles, and the scattering contribution is negligible. The sum of both contributions is called extinction cross-section σ_{ext} and is given by³⁵⁻³⁶

$$\sigma_{ext} = \sigma_{scat} + \sigma_{abs} = \frac{9\omega}{c} \varepsilon_m^{3/2} V \left(\frac{\varepsilon_r''(\omega)}{(\varepsilon_r'(\omega) + 2\varepsilon_m)^2 + \varepsilon_r''(\omega)^2} \right) \quad (1.25)$$

with V being the volume of the particle.

Figure 1.4 illustrates the influence of the nanoparticle size on the magnitude of the absorption, scattering and extinction cross-section as well as their ratios. For small silver nanoparticles ($a = 5$ nm) in air, the scattering contribution is negligible and the LSPR is almost purely determined by the absorption cross-section. As the radius of the particle is increased to 25 nm the overall intensity of the LSPR is increased by two orders of magnitude and the contribution to the extinction cross-section is shared equally between absorption and scattering. For even larger particles ($r = 50$ nm) the optical response is dominated by the scattering contribution.

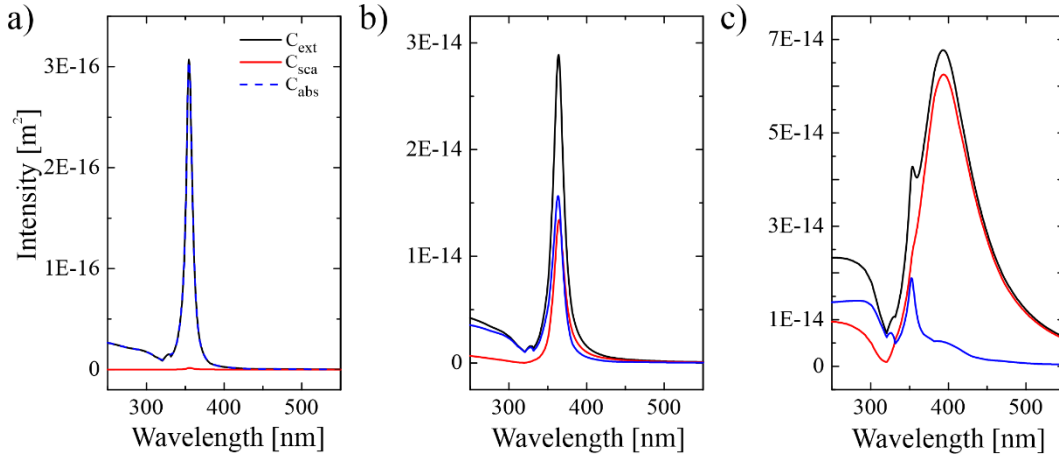


Figure 1.4 Dependence of scattering, absorption and extinction cross-section on nanoparticle size. Cross-section data of a silver nanoparticle in air with a radius of (a) 5 nm, (b) 25 nm and (c) 50 nm. The black lines represent the extinction cross-section, blue lines the absorption cross-section and the red lines the scattering cross-section. Calculated using free MiePlot software (MiePlot, www.philiplaven.com) and dielectric data from Johnson and Christy for silver.⁷⁷

For non-spherical particles, the quasi-static approximation can be extended to ellipsoids (Gans' theory) with an orientation dependent polarizability α_i along the principal axis ($i = 1, 2, 3$):³⁶

$$\alpha_i = 4\pi a_1 a_2 a_3 \frac{\epsilon_r(\omega) - \epsilon_m}{3\epsilon_m + 3L_i(\epsilon_r(\omega) - \epsilon_m)} \quad (1.26)$$

Where $a_1 \leq a_2 \leq a_3$ are the semi-axis of the particle (compare Figure 1.5 (a)) and L_i are geometrical factors.³⁶ The geometrical factors satisfy $\sum L_i = 1$ and are a function of the eccentricity e of the particle ellipsoid.³⁵

For a sphere the eccentricity is 0 and the geometrical factors are the same for all three particle axes $L_1 = L_2 = L_3 = \frac{1}{3}$.

For the approximation of a rod-shaped particle, where the short axis is described by $a_1 = a_2$, and the long axis by a_3 , the geometrical factors are $\frac{1}{3} \leq L_1 = L_2 \leq \frac{1}{2}$ and $L_3 \rightarrow 0$ as the sphere is elongated. The geometrical factor L_3 is analytically solved by:³⁵

$$L_3 = \frac{1 - e^2}{e^2} \left(-1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right) \quad (1.27)$$

With $e^2 = 1 - \frac{a_{1/2}^2}{a_3^2}$, and $L_{1/2}$ is given by:

$$L_{1/2} = \frac{1 - L_3}{2} \quad (1.28)$$

That means that the conduction electrons, oscillating along the minor and major axis, exhibit a different polarizability. Therefore, separated plasmon resonances, a transversal and a longitudinal mode, are formed as depicted in Figure 1.5 (b). The transversal mode is slightly blue-shifted when compared to a spherical particle of the same size whereas the longitudinal mode is strongly red-shifted. This red-shift scales linearly with increasing charge separation i.e. a decreasing net restoring force.

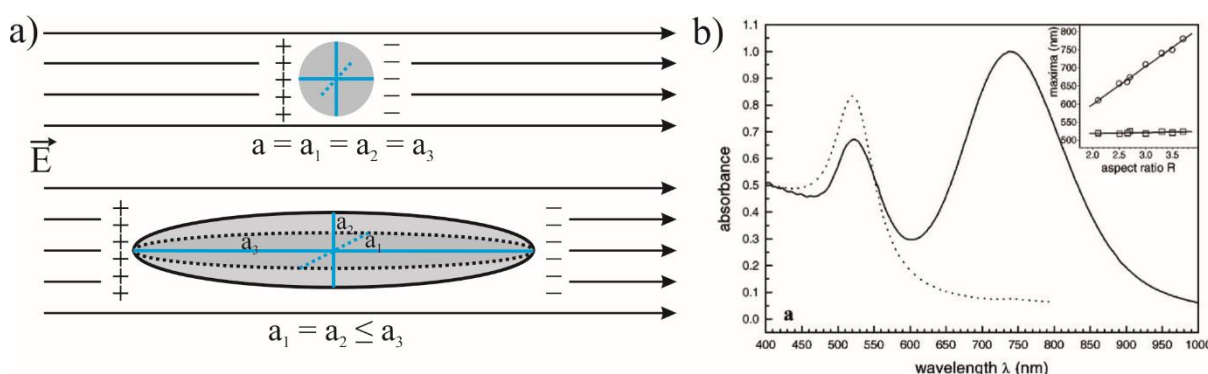


Figure 1.5 Shape-dependence of LSPR. (a) Charge separation of the conduction electrons in a spherical metal nanoparticle (top) and a rod-shaped metal nanoparticle (bottom) placed in an external electric field. (b) Comparison of a spherical Au nanoparticle with $a = 22$ nm and an Au nanorod having an aspect ratio of 3.3. The inset shows the development of the transverse (short axis, squares) and the longitudinal (long axis, spheres) surface plasmon mode with the aspect ratio. (b) Reprinted with permission from Ref. ⁴². ©2003 Annual Reviews.

The theory of scattering and absorption of radiation by small spheres predicts resonant field enhancement due to the resonance of the polarizability, if the Fröhlich condition is satisfied. For larger particles ($a > 20$ nm), this quasi-static approximation cannot be employed anymore. In addition to the dipolar resonance, multipolar modes are excited because there is a significant phase-change of the driving field over the particle volume. This causes retardation effects,

which are considered in the Mie theory.³⁶ For a metal sphere, the polarizability according to Mie theory is described by⁷⁹⁻⁸⁰

$$\alpha_{Mie} = \frac{1 - \frac{1}{10}(\varepsilon_r(\omega) + \varepsilon_m)x^2 + O(x^4)}{\left(\frac{1}{3} + \frac{\varepsilon_m}{\varepsilon_r(\omega) - \varepsilon_m}\right) - \frac{1}{30}(\varepsilon_r(\omega) + 10\varepsilon_m)x^2 - i\frac{4\pi^2\varepsilon_m^{\frac{3}{2}}V}{3\lambda_0^3} + O(x^4)}V \quad (1.29)$$

where $x = \frac{\pi a}{\lambda_0}$ is the size parameter, linking the particle radius a with the free space wavelength λ_0 . In the numerator, the x^2 term describes the effect of retardation of the exciting field over the volume of the particle. The x^2 term in the denominator on the other hand describes a retardation caused by the depolarization field inside the particle. For Drude metals like noble metals this results in an overall redshift of the dipole resonance with increasing particle size. This can be explained by the increasing charge separation when the particle size increases and thus the restoring force decreases. Due to this red-shift the effects of the interband transitions decrease as the plasmon resonance moves away from the interband transition edge. In addition, the quadratic term in the denominator increases the magnitude of polarization and therefore reduces the influence of absorption. The purely imaginary part in the denominator counteracts the increase of polarization and describes radiation damping. This damping is the main reason for the weakened dipolar mode as the particle volume increases and occurs due to a direct radiative decay route of coherent electron oscillations into photons. This is also responsible for the broadening of the plasmon resonance in larger particles. The higher order O-terms in the numerator and denominator account for higher order plasmon resonances. Consequently, the Mie theory presents a rigorous solution for the scattering and absorption of spherical plasmonic particles of arbitrary size and was even empirically extended to ellipsoidal structures by Kuwata *et al.*⁷⁹

Figure 1.6 depicts spectra showing the dependence of the plasmon resonance on various parameters. In (a) and (b), the influence of the employed dielectric function data is demonstrated.⁸¹ When the dielectric function $\varepsilon_r(\omega)$ of gold is determined using the Drude model (red lines, ε_D), a good match to the experimental data (dotted line) can be found for the real (a, top) and imaginary (a, bottom) part of $\varepsilon_r(\omega)$ between 600 nm and 1200 nm. Below that wavelength a strong deviation is observed due to the interband transitions. When the Drude-Lorentz model with one damping term is employed (blue traces, ε_{D-L}) the experimental data can be fitted down to almost 400 nm. The addition of one damping term leads to an almost perfect match of the DL-calculated extinction spectrum (blue trace, depicted in b) compared to

the spectrum calculated with experimental dielectric function data (black trace) and also to an experimentally recorded spectrum (green dotted line). When the dielectric function from the Drude model is employed instead, the resonance position appears at much shorter wavelengths because of the failure of the Drude model at short wavelengths, where it underestimates the real and imaginary parts of the dielectric function. Employing experimentally determined dielectric functions for gold⁷⁷ and silver⁷⁷, the dependence of the LSPR on the nanoparticle radius in aqueous medium was calculated using Mie theory and the results are shown in (c) and (d), respectively.

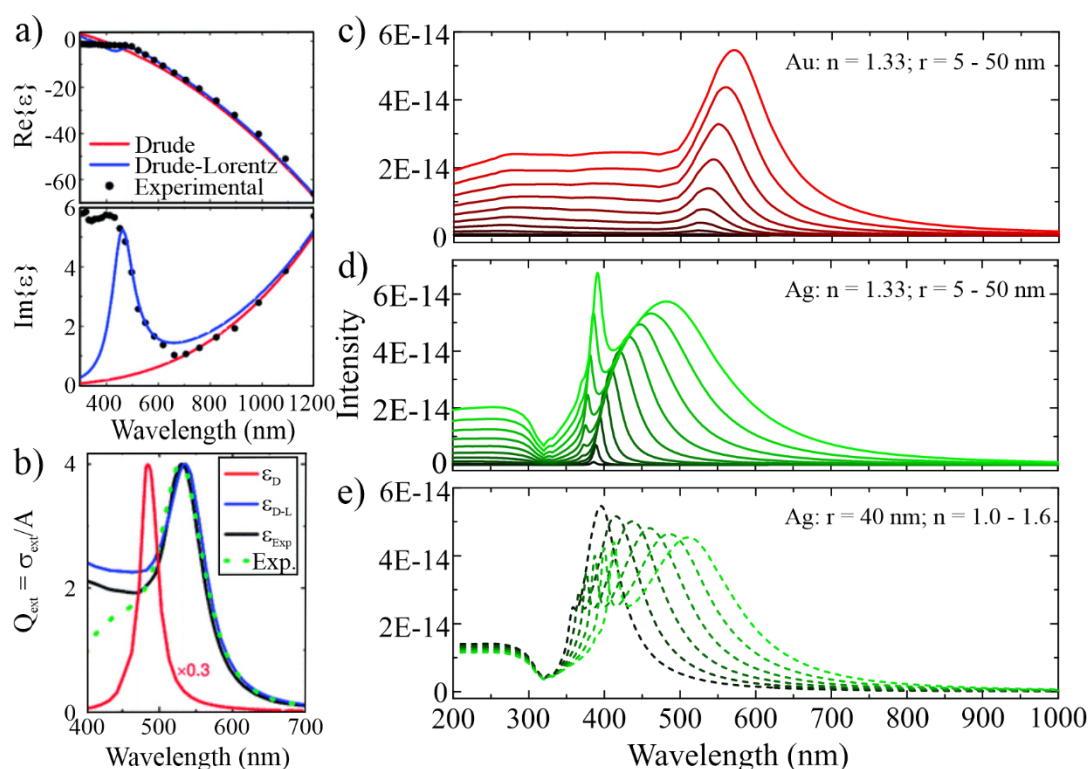


Figure 1.6 Influence of the dielectric function data on calculated gold and silver nanoparticle spectra using Mie theory. (a) Real (top) and imaginary (bottom) part of the dielectric function of gold determined using the Drude model (red line), the Drude-Lorentz model (blue line) and experimental data (black dotted line). (b) Extinction spectra of a gold nanoparticle ($r = 25$ nm) in water calculated using the dielectric function data depicted in (a) and an experimentally measured particle spectrum (green dotted line). (c) Particle size dependence of the LSPR of a gold nanoparticle in water at 20 °C ($n = 1.33$) shown for an increasing particle radius from 5 nm to 50 nm in 5 nm steps (black to red lines). (d) Particle size dependence of the LSPR of a silver nanoparticle in water ($n = 1.33$) shown for an increasing particle radius from 5 nm to 50 nm in 5 nm steps (black to green lines). (e) Dependence of the LSPR of a silver nanoparticle ($r = 40$ nm) on the surrounding refractive index environment. The refractive index n is increased from 1.0 to 1.6 (black to green dotted lines). (a) and (b) adapted with permission from Ref. ⁸¹. ©2011 American Chemical Society. The spectra in (c) to (e) were calculated using a free Mie theory calculator (MiePlot, www.philiplaven.com) and dielectric function data from Johnson and Christy.⁷⁷

A steady red-shift of the LSPR accompanied with an increase in extinction cross-section is observed for both particle types. For increasingly large silver nanoparticles, the occurrence of a quadrupolar mode around 400 nm can be observed additionally. In (e), the influence of the surrounding dielectric medium is shown for silver nanoparticles with $a = 40$ nm. As ε_m increases from 1.0 to 2.6 ($\equiv n = 1.0$ to 1.6), the LSPR continuously red-shifts and at the same time the resonance width increases significantly.

Another approach to determine the effective polarizability of larger particles is the modified long wavelength approximation (MLWA), which also accounts for the dynamic depolarization, i.e. the role of retardation across the particle and radiation damping effects. α_{MLWA} is defined by^{44, 82}

$$\alpha_{MLWA} = \frac{\alpha_{static}}{\left(1 - \frac{2}{3}ik^3\alpha_{static} - \frac{k^2}{a}\alpha_{static}\right)} \quad (1.30)$$

with a being the semiaxis of the particle parallel to the incident electric field, $k = nk_0 = \frac{2\pi n}{\lambda}$ being the wave number in a homogeneous surrounding medium, which has a refractive index $n = \sqrt{\frac{\varepsilon}{\varepsilon_0}}$. α_{static} describes the polarizability obtained from the quasi-static approximation. This simplified expression is widely employed in literature and often used for the characterization of the optical response of particles in nanoparticle arrays. The term $\frac{2}{3}ik^3\alpha_{static}$ describes the dynamic depolarization and the term $\frac{k^2}{a}\alpha_{static}$ the radiative damping.⁶⁵

1.1.2 Collective Plasmon Modes

As shown, the plasmon resonance of single plasmonic nanoparticles can be tuned in wavelength by varying size, shape and refractive index environment of the nanoparticle. A further manipulation can also be achieved by near-field or far-field coupling of multiple particles. For near-field coupling the nanoparticles are placed in close proximity to each other. This leads to an overlap of the electric fields of the plasmon resonances of the particles and induces a significant spectral shift. An example is presented in Figure 1.7, where the extinction of two silver nanoparticles with diameters d of 20 nm is depicted at particle spacings ranging from 1 to 50 nm. When the exciting light is polarized along the dimer axis (a), constructive interference occurs. This leads to an intense electric field in between the particles as shown in (c) for a gap size of 5 nm. The additively interacting dipoles lead to a red-shift of the LSPR as the interparticle distance decreases from 50 nm to 1 nm (e). However, light polarized perpendicular to the dimer axis (b) leads to destructive dipole interference and therefore a less intense electric

field within the gap (d). Spectrally this results in a blue-shifting LSPR as the interparticle distance decreases (f).

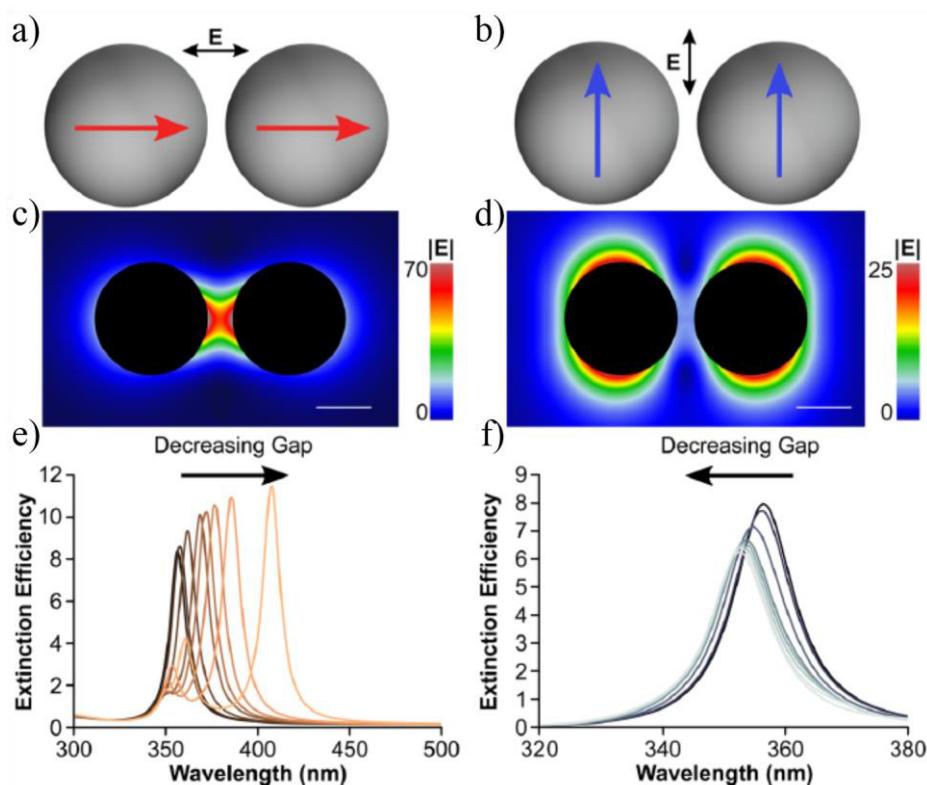


Figure 1.7 Near-field plasmon coupling in spherical particle (Ag nanoparticle, $d = 20$ nm) dimers with small interparticle gaps.⁸³ (a) Constructive dipolar coupling when the exciting light is polarized along the dimer axis. (b) Destructive interference between the dipoles when light polarized perpendicular to the dimer axis is used. (c) Electric field intensity between two constructively interfering particles separated by a 5 nm gap. (d) Electric field intensity of the same particles under destructive interference. Extinction spectra of the particle dimers with decreasing gap sizes with light polarized parallel (e) and perpendicular (f) to the dimer axis. The largest gap size is 50 nm (darkest trace) and decreases stepwise (40 nm, 30 nm, 20 nm, 10 nm, 5 nm, 4 nm, 3 nm, 2 nm) down to 1 nm (lightest trace). The scale bar is 10 nm. Reprinted with permission from Ref. ⁸³. ©2015 American Chemical Society.

For far-field coupling, particles are arranged into two dimensional arrays. Typically, the studied regular particle arrays possess Bragg modes λ_{Bragg} within the wavelength range of the plasmon resonance of the single particle. Only under these conditions, coupling resonances can occur at wavelengths slightly longer than the Bragg mode, whose wavelength depends on the lattice period and the refractive index environment. The originating coupled modes are called surface lattice resonances (SLR) and are spectrally much narrower than the single particle resonance of the respective particle. This behavior is the result of radiative plasmon coupling. Due to their narrow bandwidth accompanied by longer lifetimes and their high sensitivity, these resonances are of high interest for nanophotonic applications like sensors and nanophotonic lasers.

Before such SLRs were found in experimental works, their existence was predicted in several theoretical works for example by Schatz⁸⁴⁻⁸⁷, Markel⁸⁸⁻⁹⁰ and Carron⁹¹. They provided design rules that could lead to ultra-narrow linewidths of below 1 nm. Most often, the coupled dipole approximation (CDA) is used to describe the coupling between the nanoparticles in an array. Here, every particle is treated as a single dipole resonator that possesses a certain polarizability α depending on material, size and shape (compare section 1.1.1). When an incoming electromagnetic wave excites the resonances of the particles in the lattice, they all oscillate in phase and form a standing wave pattern in the lattice plane. Then, the diffractive scattering of the photons at each particle can excite resonances in the adjacent particle instead of decaying into free space. This leads to a suppression of radiative losses in lattice resonances.⁶⁶ In an infinite lattice of identical particles, it can be assumed that the induced polarization in each nanoparticle is the same and an effective array polarization α_{eff} can be determined. It is defined by an array factor S (also referred to as dipole sum), which depends on the geometry of the lattice and describes how the dipoles of the adjacent particle influence the polarizability of the single particle α_{MLWA} (equation 1.30).^{39, 44, 64, 83} Instead of α_{MLWA} , also polarizabilities calculated with other models like the quasi-static approach (for small particles) or Mie theory (exact solution) can be employed.

$$\alpha_{eff} = \frac{1}{\frac{1}{\alpha_{MLWA}} - S} \quad (1.31)$$

with

$$S = \sum e^{ikr_j} \left[\frac{(1 - ikr_{ij})(3\cos^2\theta_{ij} - 1)}{r_{ij}^3} + \frac{k^2 \sin^2\theta_{ij}}{r_{ij}} \right] \quad (1.32)$$

θ_{ij} is the angle between the vector r_{ij} , i.e. between dipole i to dipole j , and the direction of the polarization, induced by the incident electric field. The extinction cross-section of one particle in the array can then be calculated again by $C_{ext} = 4\pi Nk \text{Im}(\alpha_{eff})$.⁶⁴ When the real parts of $\frac{1}{\alpha_{MLWA}}$ and S are equal, the real part in the denominator in equation (1.31) approaches zero and consequently the effective polarizability of a particle becomes very large. This is precisely the resonance condition for a surface lattice resonance and is similar to the Fröhlich condition in single particle LSPRs. In nanoparticle arrays, where we have the additional effect of the dipole sum, which depends on the array parameters, an additional degree of freedom for the improvement of the quality of the plasmonic mode is available. Here, the intensity and width

of the SLR is governed by $\text{Im}\left(\frac{1}{\alpha_{MLWA}} - S\right)$, which becomes small when $\text{Im}\left(\frac{1}{\alpha_{MLWA}}\right)$ is compensated by $\text{Im}(S)$.⁴⁵ This effect is shown in Figure 1.8 (a) and (b) where a strong and narrow resonance is only observed when both imaginary terms are negative and of similar magnitude. At the second crossing point of the real parts (at lower wavelength), the imaginary parts are of opposite signs and thereby contribute additively to the polarizability and therefore the damping increases. Consequently, only a broad SLR with lower intensity is formed at this wavelength. Calculations and experiments have shown that the SLR are most intense and narrow when the diffraction edge lies in close proximity to the single particle resonance.^{44-45, 92} Therefore, this phenomenon is sometimes termed diffraction coupled localized plasmons. Whether this diffraction edge lies on the high energy side of single particle LSPR (smaller wavelength, Figure 1.8 (c) upper inset) or on the low energy side (larger wavelength, main spectrum Figure 1.8 (c)) has a significant effect.

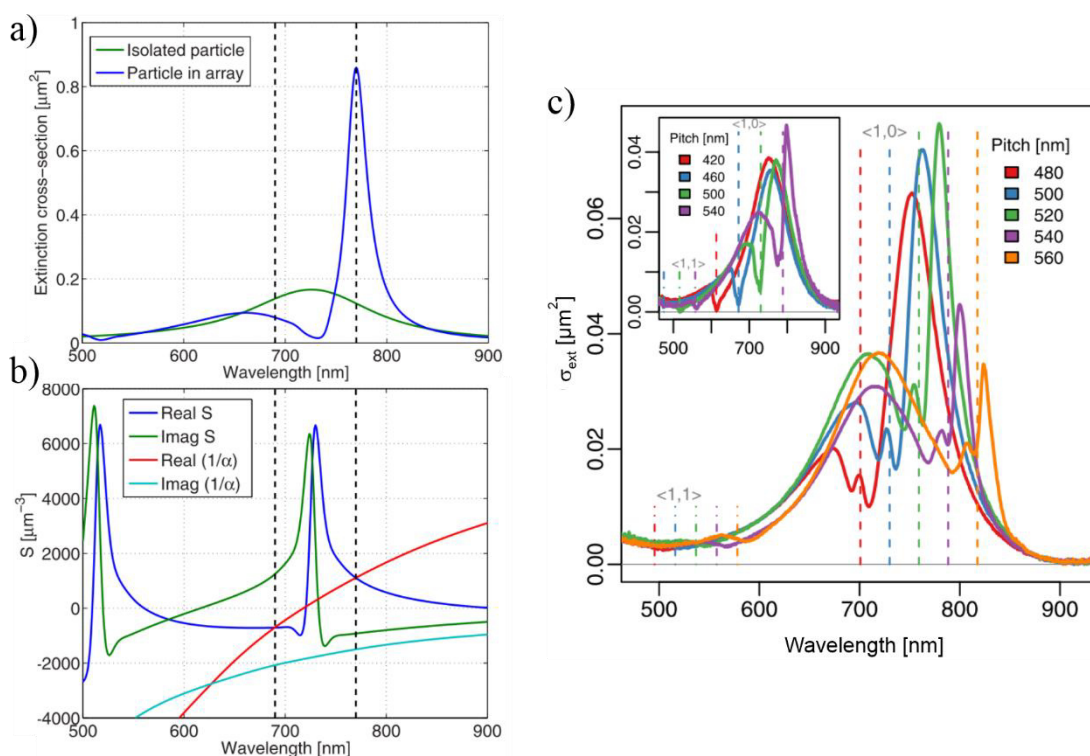


Figure 1.8 Comparison of LSPR and SLR and dependence on α and S . (a) Calculated extinction cross-section per particle for a single silver nanodisc ($d = 120$ nm, $h = 30$ nm; green trace) and a square array of these particle (480 nm pitch; blue trace) and (b) the real and imaginary part of the single particle polarizability and the array factor of the square array. The dashed black lines in both plots indicate the intersection of the real parts of $1/\alpha$ and S . The particle response is approximated by MLWA theory and the surrounding refractive index is $n = 1.515$.⁴⁵ (c) Effect of diffraction edge position with respect to LSPR maximum.⁴⁴ (a,b) Reprinted with permission from Ref.⁴⁵ ©2014 American Physical Society. (c) Reprinted with permission from Ref. ⁴⁴. ©2008 American Physical Society.

On the high-energy side of the LSPR, the diffracted order is of higher energy than the particle LSPR and therefore only very little radiative coupling can occur. A Fano-type shape results from interference between directly transmitted light and the light scattered by the array. Here, the main resonance is red-shifted, enhanced and sharpened compared to the single particle response. When, however, the diffraction edge lies on the low-energy side of the plasmon resonance, a very intense and sharp resonance occurs in the long-wavelength tail of the main resonance due to efficient radiative coupling.

A closer theoretical look at the effect of the array period on the optical response of spherical silver nanoparticles was presented by Zou *et al.*⁸⁴ They employed the dipole sum approach to calculate the extinction efficiency (ratio of extinction cross-section to geometrical area) of particle arrays with periods between 200 nm and 700 nm and up to 400 particles. Their results are shown in Figure 1.9 for 1D chains in (a) and for 2D hexagonal arrays in (b). As a reference, the single particle response is shown in (a) as dotted line. For both types they found SLRs which shift steadily to longer wavelengths as the period increases. In the 1D case, the resonances were particularly narrow and the strongest resonance at 470 nm spacing showed a FWHM of 3.7 nm. The resulting Q-factor was 135, which is 10 times higher than the Q-factor of the single particle resonance. Larger distances lead to even higher Q-factors but at the same time, the intensity of the resonance decreased significantly.

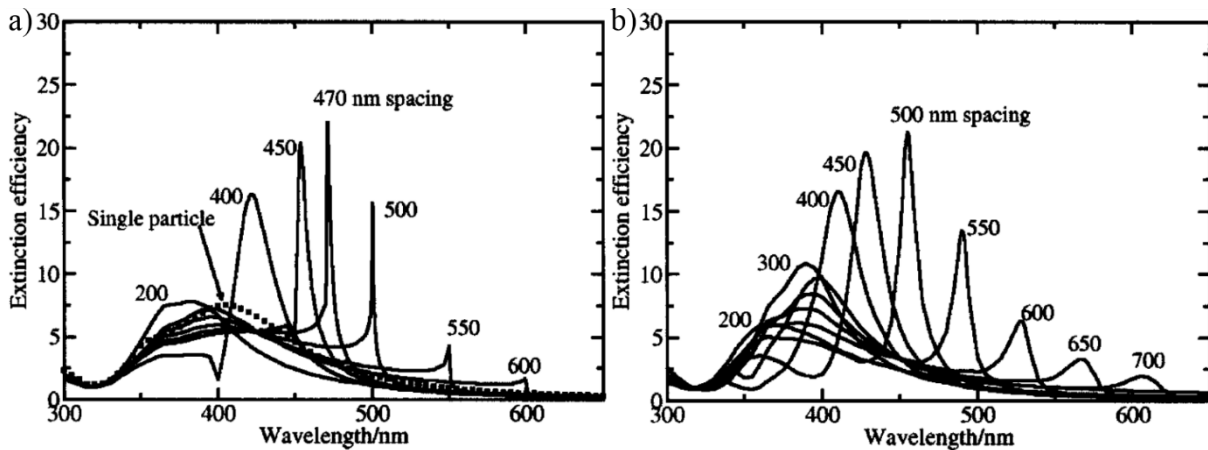


Figure 1.9 Extinction spectra of silver nanoparticles with $a = 50$ nm in (a) a 1D chain of 400 particles and (b) a 2D hexagonal array of 400 particles with a particle spacing between 200 and 700 nm. Reprinted with permission from Ref. ⁸⁴. ©2004 American Institute of Physics.

Comparing this to the results of the 2D array, which showed the same general behavior but overall broader resonances, one would prefer 1D arrays over 2D arrays. However, only in 2D arrays the existence of SLRs could be demonstrated experimentally so far. In 2008, Kravets *et al.*⁹³ were the first to show pronounced SLRs in gold dimer arrays via spectroscopic

ellipsometry. A first attempt using gold nanopillars with a height of $h = 90$ nm and a diameter of $d = 100$ nm in a 2D square array with a period of 320 nm failed due to insufficient overlap of the LSPR mode and the Rayleigh scattering wavelength at 600 nm at an angle of incidence between 62° and 68° . Using dimers instead of single nanopillars dipole-dipole coupling lead to the formation of blue and red-shifted modes. The blue-shifted resonance (from 700 nm to 600 nm) possessed the correct wavelength, enabling the coupling between the diffractive mode and the LSPR resulting in the first observed SLRs.

Auguie and Barnes shortly after used a different method to realize an overlap between the LSPR and the Rayleigh wavelength. The array periodicity as well as the particle size of a square gold nanoparticle array was tuned.⁴⁴ The samples with total dimensions of $35 \times 35 \mu\text{m}^2$ were prepared using electron beam lithography on fused silica substrates. For an array using particles with dimensions of ($h = 100$ nm, $l = 90$ nm, $w = 35$ nm) and a period of 480 to 560 nm, SLRs were recorded in transmission geometry when illuminated at normal incidence and placed into a homogeneous refractive index environment (immersion oil, $n = 1.46$, Figure 1.10 (a) top). The LSPR of the single particle is located at 710 nm and as the diffraction edge sweeps through the LSPR a narrow SLR shifts to longer wavelength as the period increases. The intensity of the SLR depends on the overlap between the propagation field (diffraction) and the localized plasmon resonance.

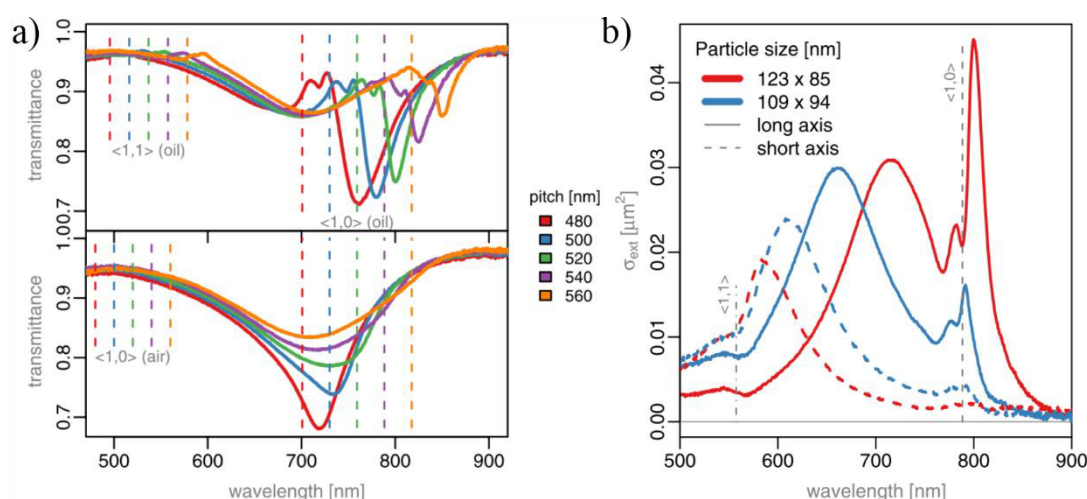


Figure 1.10 Dependence of the SLR on nanoparticle period and refractive index environment. (a) Transmittance spectra of Au arrays in homogeneous refractive index environment (light through immersion oil, top) and in asymmetric refractive index environment (light through air, bottom) with period ranging from 480 to 560 nm. The vertical lines indicate the $\langle 1,0 \rangle$ and $\langle 1,1 \rangle$ diffraction edges in oil and air. (b) Extinction spectra for polarization along the long axis (solid lines) and the short axis (dashed lines) of two particle arrays with the same pitch of 540 nm but different particle aspect ratios. Reprinted with permission from Ref. ⁴⁴. ©2008 American Physical Society.

This dependence on the overlap becomes particularly obvious in Figure 1.10 (a), where the transmission spectra were converted into spectra showing the extinction per particle. As long as the diffraction edge is located at the lower energy side of the LSPR (above 710 nm), the SLR is more intense when a larger overlap (close to the LSPR) is realized. When however, the diffraction edge is located at the tail of the LSPR a still narrow but less intense SLR is observed (pitch 560 nm).

Additionally, it was shown that not only the diffraction edge can be tuned through a particle LSPR but also the other way round.⁴⁴ The LSPR position depends on the polarizability of the particle, which is determined by the size, shape and material of the particle. In the present case the particle material and especially volume was kept constant but the aspect ratio (i.e. shape) of the nanorods in the array was varied. This led to a much more pronounced SLR in the case of the particles with a higher aspect ratio, due to a better overlap of its LSPR and the chosen diffraction edge (Figure 1.10 (b)).

In a second set of experiments, arrays with the same period as in the first case (index matched with oil) are placed in an inhomogeneous refractive index environment (Figure 1.10 (a) bottom, air as superstrate). Only one asymmetric peak is formed and no SLRs can be observed. Here no coupling between the LSPR and diffraction edge takes place because the asymmetry between the substrate and superstrate hinders the radiative coupling. Later it was shown by Chu *et al.* that the homogeneity of the surrounding RI does not have to be perfect.⁹⁴ For Au nanoparticle arrays with different periods index matching with water ($n = 1.33$) for a glass substrate ($n = 1.56$) was sufficient for the formation of SLRs.⁹⁴ B. D. Thackray *et al.*⁹⁵ explored the potential to use arrays with different particle geometries and lattice constants for biological and chemical sensing applications. He systematically varied the refractive index environment from air, over water to glycerol.

For the formation of SLRs another important parameter is the lattice size required for the formation of a diffractive mode which is strong enough to couple to the single particle LSPR. A study conducted by Rodriguez *et al.* used the coupled dipole approximation and experiments to show the dependence of the quality factor of the SLR Q_{SLR} on the array size.⁶⁵ Rectangular arrays (lattice constants $a_x = 500$ nm and $a_y = 300$ nm) of gold nanodisks ($d = 120$ nm, $h = 50$ nm) were prepared with an increasing number of particles N in x - and y - direction. $N \times N$ was tuned starting with 2×2 lattices up to 10×10 lattices in experiment and up to 30×30 in the calculations. Figure 1.11 (a) shows that already in 5×5 lattices weak SLRs can be distinguished in the experiment as well as in the simulation. The resonance around 790 nm steadily increases

in intensity and becomes narrower as the array size further increases. The resonance position depends only weakly on the array size. A second feature, which forms at around 710 nm in the experiment, was attributed to a poorly collimated incoming light beam. The calculated spectra, which are the result of an angular averaged response for $\theta_{\text{inc}} = 0^\circ$ to $\theta_{\text{inc}} = 6^\circ$, support this reasoning. Interestingly, this second feature is also visible in the work of Augu   and Barnes presented above and in several other works.^{43-44, 93, 96} Focusing on the impact of the array size on the quality of the SLR, the quality factor was calculated for arrays between 2×2 and 30×30 as well as for a single particle and an infinite array (Figure 1.11 (b)). By doing so, they were able to identify three different regimes for Q_{SLR} : (i) for $N \leq 5$, the quality factor of the single particle LSPR (Q_{LSPR}) is higher than for the lattice mode (Q_{SLR}); (ii) for N between 5 and 20, Q_{SLR} increases rapidly; and (iii) for $N > 20$, Q_{SLR} starts to saturate, and slowly approaches $Q_\infty = 30$ of the ‘infinite’ array. This shows that already rather small lattices are able to support SLRs and that arrays of only of a few hundred particles can be assumed to be ‘infinite’.

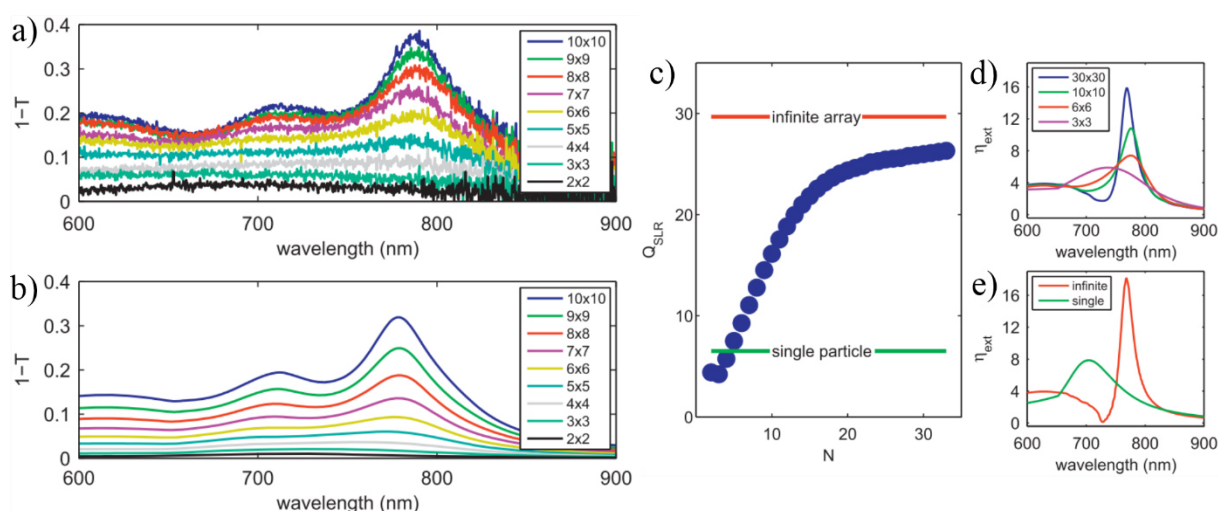


Figure 1.11 Influence of array size on SLR in homogeneous refractive index environment. (a) Extinction spectra of rectangular gold nanoparticle discs (lattice constants $a_x = 500$ nm and $a_y = 300$ nm, $d = 120$ nm, $h = 50$ nm) with $N \times N$ particles with N ranging from 2 to 10. Top: experimental data. Bottom: Coupled dipole model calculations. (b) Calculated Q_{SLR} of the SLR as function of the number of particles N . Reprinted with permission from Ref. ⁶⁵.   2012 American Physical Society.

Another parameter that can be easily tuned in lithographically prepared samples is the lattice geometry of the plasmonic arrays. Humphrey and Barnes studied silver square, rectangular, hexagonal and honeycomb arrays under normal incident light and compared the experimental results to theoretical results using the coupled dipole approximation.⁴⁵ It was demonstrated that the SLR position does not only depend on the diffraction edge, which was the same for the square, hexagonal and honeycomb array, and LSPR position but slightly different resonance positions were obtained for the different geometries. This difference was explained by different

intersections of the real part of the inverse polarizability $1/\alpha$ and the array factor S shown in Figure 1.12 (c). As all three structures show a high degree of symmetry the optical response is only weakly dependent on the polarization of the incoming electric field. In contrast to that, a rectangular particle array exhibits an optical response, which is strongly dependent on the polarization. Only when the incident beam is polarized along the x-axis of the particle array and is matching the LSPR wavelength, a SLR is formed as shown in (b) and (d). In y-direction a different lattice spacing is prevailing. This leads to a different array factor S and a diffraction edge, which is not matched to the particle LSPR. Consequently, no coherent coupling takes place.

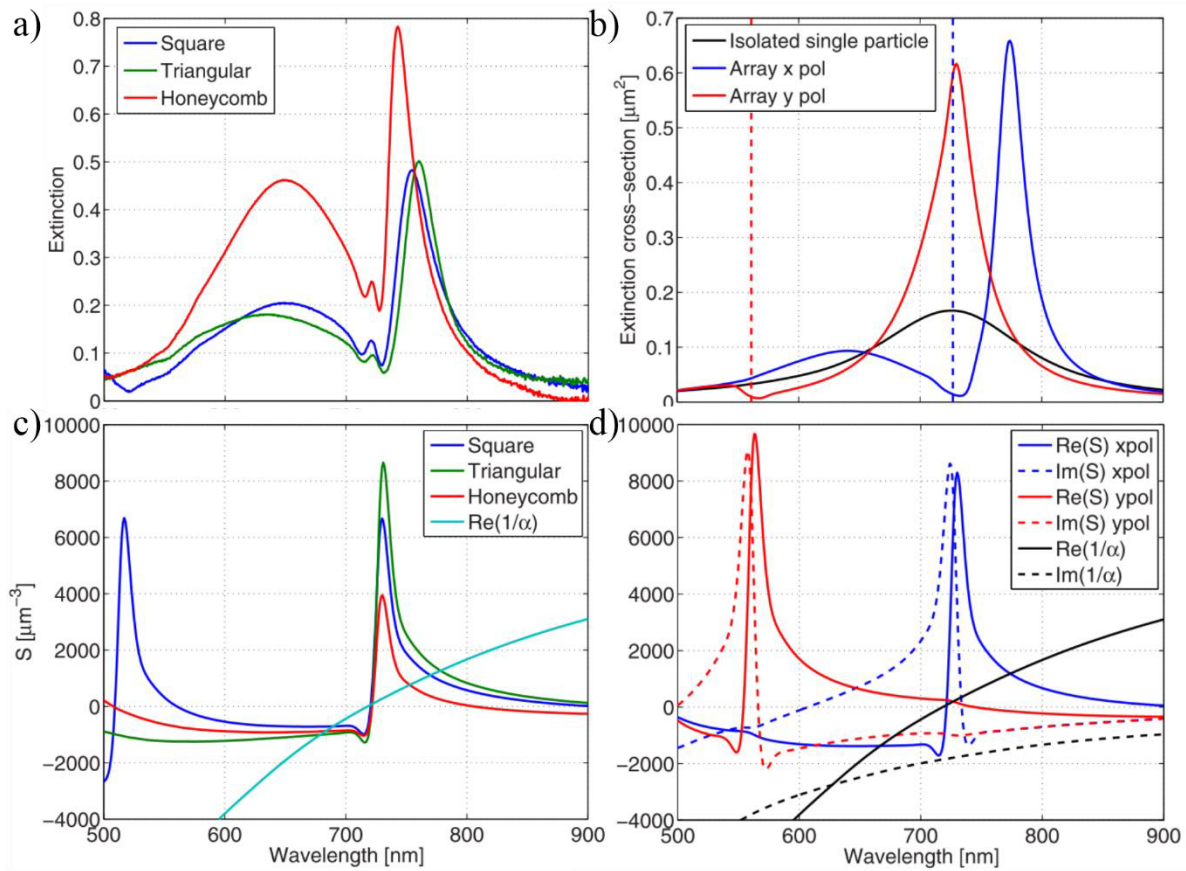


Figure 1.12 Influence of the lattice geometry on the SLR. (a) Experimental extinction spectra of silver particle ($d = 120$ nm, $h = 30$ nm) arrays with a square lattice (blue line), triangular lattice (green trace) and a honeycomb lattice (red trace) with the same diffraction edge and illuminated with linearly polarized light. (b) Calculated extinction spectra of a rectangular silver particle array (370 nm $\times$ 480 nm pitches) illuminated with polarized light along the x-axis (blue trace) and the y-axis (red trace). The dotted lines show the respective diffraction edge. (c) Real parts of the array factor S of the lattices shown in (a) and the real part of $1/\alpha$. (d) Real and imaginary parts of the array factor and $1/\alpha$ of a rectangular lattice in dependence of the polarization direction of the illuminating light employed in (b). Reprinted with permission from Ref. ⁴⁵. ©2014 American Physical Society.

In a more recent study, Guo *et al.* demonstrated a much more pronounced effect of lattice geometry at off-normal incidence.⁴⁷ The SLRs show a strongly dispersive behavior, which depends on the polarization of the incoming E-field. As the angle deviates from normal incidence the diffractive order vector changes and consequently its orientation towards the dipoles of the particles is changed. This leads to a dispersive behavior, as depicted in Figure 1.13 (a) and (b) for square lattice and the occurrence of multiple resonance features shifting away from the starting wavelength at normal incidence as the angle of incidence increases. The dispersive behavior is only pronounced when the incoming light is polarized perpendicular (TE) to the in-plane wave vectors in the y direction.

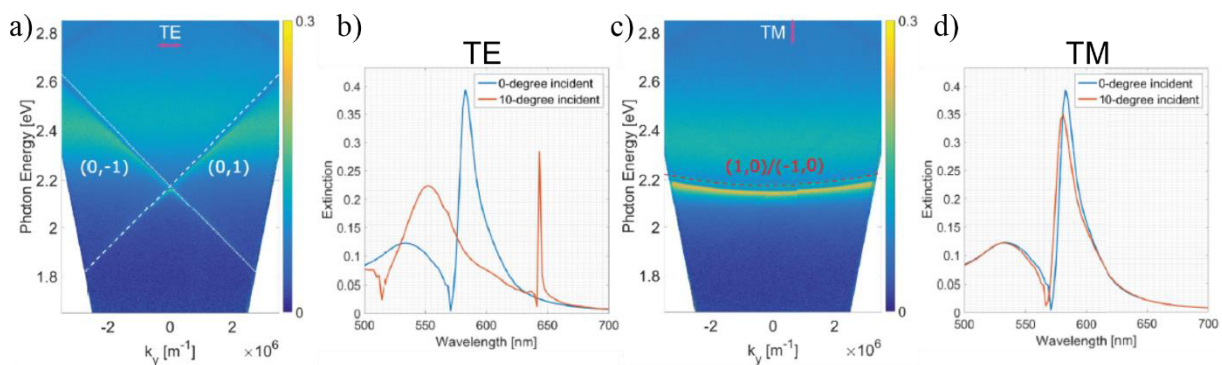


Figure 1.13 Polarization and angle dependence of the optical response of a square lattice of silver nanoparticles ($d = 60$ nm, $h = 30$ nm). Angle dependent extinction spectra for (a) TE and (c) TM polarized light. The dashed white line represents the calculated (0,1) diffractive order and the dotted white line the (0,-1) diffractive order. The dashed red line describes the calculated degenerate diffractive orders (1,0) and (-1,0). The broad, angle independent feature around 2.4 eV is the LSPR and the dispersive feature following the diffractive orders is the SLR. FDTD simulated extinction spectra for the square lattice under normal and 10° incident light with (b) TE and (d) TM polarization. Reprinted with permission from Ref. ⁴⁷. ©2017 American Physical Society.

Furthermore, the effect of a superlattice was explored by Wang *et al.* using hierarchical Au nanoparticle arrays, with a certain nanoparticle periodicity as well as a patch periodicity.⁵⁰ Like this ultranarrow superlattice plasmon resonances were formed by coupling of the single-patch lattice plasmons to Bragg modes of different orders originating from the patch periodicity. Consequently, the superlattice plasmon resonance can be tuned either by varying the patch periodicity or the nanoparticle periodicity.

Another important parameter, especially for the preparation of self-assembled lattices, which is the aim of this thesis, is the effect of disorder. Theoretically, this was already investigated for 1D chains in 2006 and 2007 by Zou *et al.*⁸⁷ and Markel *et al.*⁹⁰, respectively. Experimental results for 2D square arrays prepared by e-beam lithography were presented in 2009 by Auguie and Barnes.⁴³ Here, certain distributions of particle positions ranging from ordered, partially

disordered (10 % to 40 %) and pseudo-random were studied in nanorod (120 nm x 80 nm x 35 nm) arrays with total dimension of 35 μm x 35 μm (examples see Figure 1.14 (a)-(c)). Additionally, the effect of particle polydispersity was investigated (examples see Figure 1.14 (d) and (e)) and all results were compared to theoretical spectra obtained using a coupled dipole model.

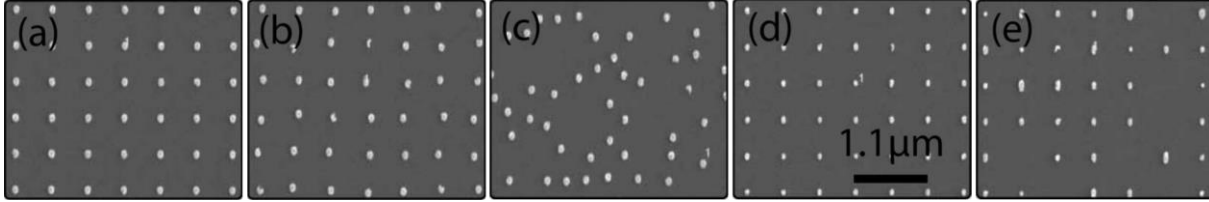


Figure 1.14 Samples prepared by e-beam lithography and thermal deposition to study the effect of positional disorder and particle polydispersity on SLRs. The square arrays had a total size of 35 μm x 35 μm , a period of 550 nm and the particles were gold nanorods with dimensions of 120 nm x 80 nm x 35 nm. (a) ordered array. (b) 10 % deviation of nominal regular separation. (c) pseudo-random array. (d) 10 % variation in length of the long-axis of the nanorod and (e) 100 % variation in length of the long axis. Reprinted with permission from Ref. ⁴³. ©2009 Optical Society of America.

Figure 1.15 (a) presents the experimental (top) and calculated (bottom) extinction spectra of five different nanorod arrays that only differ in positional order. The ordered array (red traces) shows a narrow SLR red-shifted to the <1,0> diffraction edge and a broad LSPR on the higher energy side. As the particles are displaced randomly but to a controlled extent (20 %, 30 %, 40 % and pseudo-random) the optical response changes dramatically. The SLR blue-shifts continuously towards the diffraction edge and simultaneously the resonance intensity decreases significantly because the strength of the coherent coupling between the particle dipoles is weakened. At the same time the exact opposite behavior is seen for the LSPR - the resonance red-shifts and increases in intensity until the single particle LSPR is the only spectral feature left in the pseudo-random array. These observations are valid for the experimental as well as for the calculated spectra. The spectral features obtained from calculations are in general more narrow than the ones from experiment, since in the calculations the effect of surface roughness, refractive index inhomogeneities (chromium underlayer) and deviations from the nominal particle sizes are neglected. The effect of particle polydispersity is shown in Figure 1.15 (b) by introducing deviations in the length of the long-axis of the particles. In the nominally perfect array a pronounced and narrow SLR is again observed red-shifted from the diffraction edge and a LSPR blue-shifted from it. At 10 % polydispersity only minor change in spectral shape can be seen. However, a further increase in polydispersity leads to broader resonance features as well as a drastically decreased extinction intensity. The experimental results were confirmed by the calculated spectra shown on the right. The spectra in the bottom plot show that the same

trend of decreasing extinction intensity, increasing resonance width and red-shift of the resonance positions is also true for unassembled particles as the particle size distribution widens. This can be attributed to the various particle volumes and aspect ratios that lead to different resonance positions and extinction strengths due to a varying polarizability. The asymmetry in resonance shape as well as the overall red-shift of the resonance position is related to the higher contribution of large particles to the overall optical response than of smaller particles. In an array this distribution of LSPRs results in a less efficient coherent coupling because fewer particles support a LSPR that matches with the diffraction edge. This leads to the observed effects in experiment and calculation of decreasing resonance intensity of the SLR.

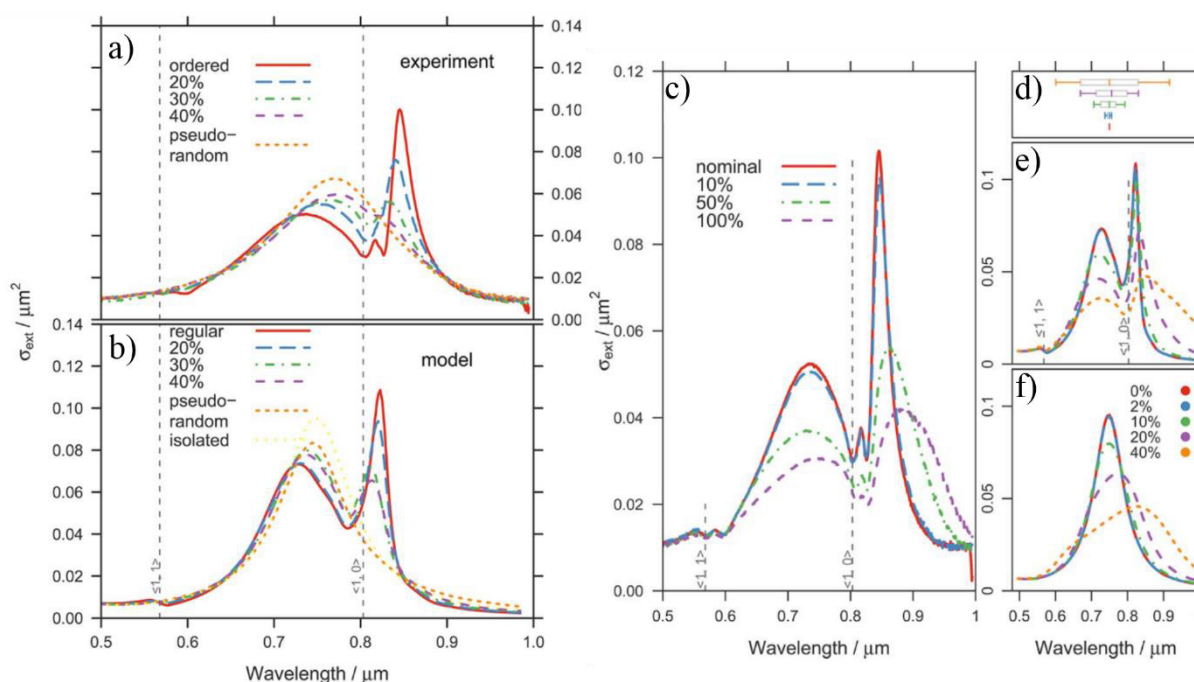


Figure 1.15 Effect of positional disorder and particle polydispersity on SLRs. (a) Measured extinction spectra of five different arrays with increasing degree of positional disorder ranging from ordered over 20 %, 30 % and 40 % of disorder to pseudo-random. The overall number of particles was kept constant. (b) Calculated extinction spectra using a coupled dipole model using the array parameters from experiment. (c) Measured extinction spectra of ordered arrays but varying particle size. The size variation was introduced to the long-axis of the particles. The results are displayed for nominally monodisperse particles, 10 %, 50 % and 100 % variation (compare (d)). (e) Corresponding calculated spectra using a coupled dipole model. (f) Calculated spectra of 441 particles with the varying polydispersity (0 – 40 %) not arranged into a lattice. In all plots the $\langle 1,1 \rangle$ and $\langle 0,1 \rangle$ diffraction edges of the periodic array are displayed as vertical dashed lines for a homogeneous RI environment of 1.46. Reprinted with permission from Ref. ⁴³. ©2009 Optical Society of America.

1.1.3 State-of-the-Art Preparation Methods of Plasmonic 2D Nanoparticle Arrays

In the experimental works presented in the previous chapter and in most other works lithographic top-down methods were employed for the preparation of plasmonic nanoparticle arrays and nanooptical devices. Due to the high precision and the reproducibility of these techniques, they are perfectly suited for fundamental investigations of the properties of such devices.⁹⁷ Popular lab methods are for example focused ion beam or electron beam lithography, which are maskless sequential techniques.⁶⁷ They are widely used to produce very accurate nanostructures of different sizes or shapes onto substrates.^{43-45, 47, 93-95, 98-100} Typically, structural feature sizes of 20 nm and even below can be produced because electron-beam lithography is not diffraction limited. The process of electron-beam lithography is schematically shown in Figure 1.16. A substrate, usually a silicon wafer or borosilicate glass, is coated with a polymeric positive or negative resist via spin-coating. Next, the resist is exposed to a focused e-beam with which the desired pattern is written into the resist. The highly energetic electrons break down the chemical bonds of the polymer (in case of a positive resist) and upon dipping the sample into a developer (solvent) the exposed resist is removed. The patterned resist can now be used for substrate doping, etching or, as desired for the metal nanoparticle preparation, coating with metal. Thermal evaporation of a metal for example will create a thin metal film on top of the resist and more importantly also in the voids. After stripping, i.e. the removal of the resist with a solvent, the final pattern is obtained.

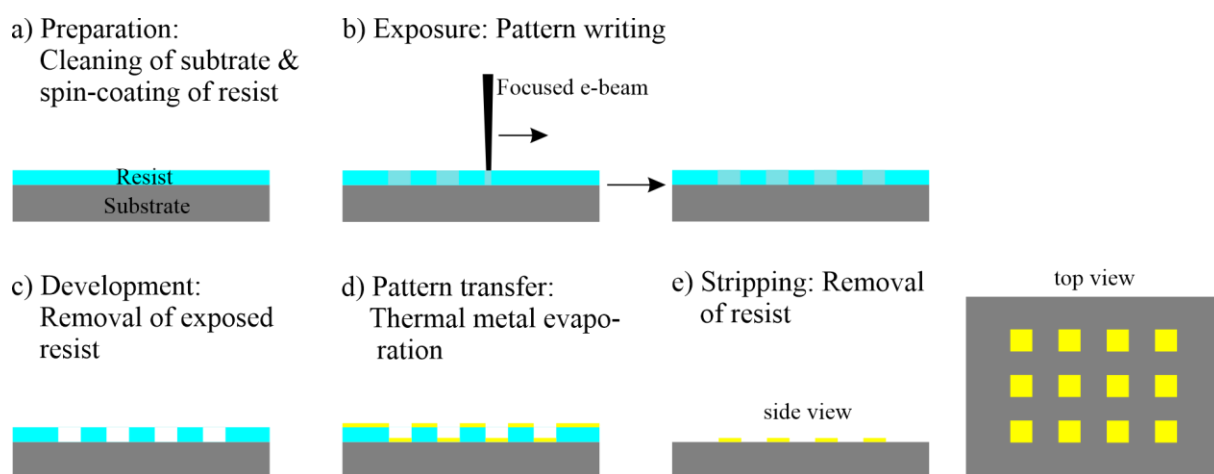


Figure 1.16 Schematic description of electron beam lithography. (a) Preparation of substrate for including cleaning and application of a resist using spin-coating. (b) Directed exposure of the resist to a focused electron beam for pattern writing. (c) Development of pattern using a solvent for the exposed areas of the resist (positive resist). (d) Pattern transfer to thermally evaporated metal film. (e) Stripping with a solvent for the resist in order to obtain desired metal pattern on substrate.

Based on this technique, soft-⁷⁰ and nanoimprint¹⁰¹ lithography have been developed where a stamp, made by electron-beam lithography, is used.⁹⁷ This technique creates structures with the same accuracy but at lower cost, since the stamp can be used multiple times.¹⁰²⁻¹⁰³ A precise pattern is transferred by mechanical contact and three-dimensional material displacement into a moldable material. This material, which serves as new mold, can be a liquid (monomer) which is hardened (cured) by temperature or UV light. After imprinting the pattern, a thin residual layer is etched off before thermal evaporation can be used again to form for example metal nanoparticles within the voids. Another technique that allows for the preparation of large, free-standing patterned surfaces via phase-shifting photolithography is called PEEL (phase-shifting photolithography, etching, electron-beam deposition, lift-off of film) and was developed by the Odom group.^{71-73, 104} A flexible approach that allows tunability in particle density, fill factors and lattice symmetries from a single master was presented by the same group and is called solvent assisted nanoscale embossing (SANE).¹⁰⁵ As schematically depicted in Figure 1.17, a master mold is used to prepare elastomeric SANE molds. These can be swollen with different solvents in order to control pattern densities and fill factors.

For the SANE process, the PDMS mold is wet with solvent and then placed onto a photoresist-coated substrate. The inverse approach (inSANE), which allows patterning of flexible substrates, uses molds that are wet with photoresist and are then placed into contact with a substrate.¹⁰⁵ Similarly, for SCIL (Surface Conformal Imprint Lithography) flexible stamps are employed to replicate the lattice pattern into a sol, which is then solidified.⁶⁰ This pattern combined with metal deposition and lift off (etching) can produce wafer-scale arrays of metal nanoparticles.⁶⁰ Consequently, SCIL, PEEL, SANE and inSANE secondary molds, prepared from a master mold, are typically used to pattern a (photo)resist. The patterned resist is then used to create metal hole arrays by evaporation. From this patterned metal film, nanoparticle arrays can next be prepared by a second metal evaporation and removal of the first metal film as shown in Figure 1.17 (b). The results are very well ordered, large scale and reproducible 2D plasmonic arrays. However, the methods suffer from a high complexity, as they require multiple preparation steps and equipment and are very time-consuming. Moreover, they deliver a rather poor particle quality.

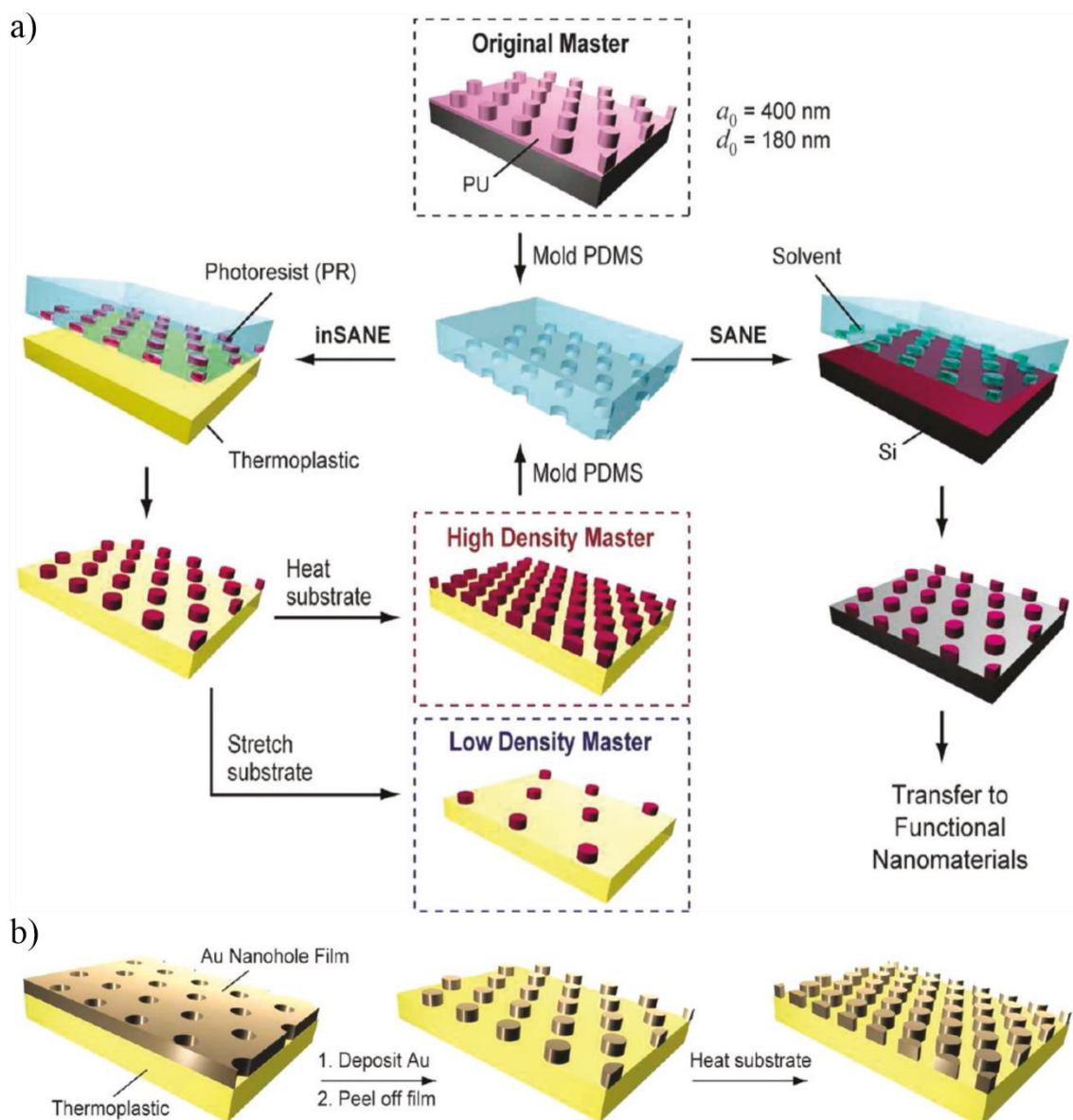


Figure 1.17 Solvent-assisted nanoscale embossing. (a) Scheme of the nanofabrication procedure to create high-density and low-density masters using inverse SANE (inSANE) and to produce patterns with features smaller than (but with the same pitch as) a master using SANE. (b) Scheme to create high-density nanoparticle arrays starting from a gold nanohole array as a deposition mask followed by heating of a shrink-film substrate. Reprinted with permission from Ref. ¹⁰⁵. ©2010 American Chemical Society.

A substantially faster way to produce nanoparticle arrays on large areas is the focus of my thesis. It is based on a bottom-up approach using wet-chemistry particle synthesis and self-assembly of those particles into 2D arrays. The particle synthesis can give access to high quality and tunable nanoparticles. These particles can then be self-assembled into ordered 2D arrays preferably on cm^2 sized sample areas. The large sample areas enable the investigation of the optical properties with far-field UV-vis absorbance spectroscopy. With these structures and

techniques, the importance of order, lattice type, material type and device environment can then be investigated and compared to lithographic approaches.

The bottom-up approach leads to two important prerequisites for my work: 1) Protocols for a nanoparticle synthesis that allows for reproducibility, monodispersity, morphology control, tunability and colloidal stability of the formed nanoparticles. 2) Assembly methods yielding high quality monolayers without aggregation, controlled interparticle spacings, and geometry. Therefore, the next three chapters will give insight into metal nanoparticle synthesis, forces in colloidal systems and assembly methods.

1.2 Nanoparticles and Colloids

According to a purely size related definition, nanoparticles are materials with outer dimensions between 1 to 100 nm (IUPAC, ISO).¹⁰⁶⁻¹⁰⁷ This definition is sometimes softened to the requirement that only one dimension has to be in this size range (EU). Nanoparticles can consist of any material such as metals, semiconductors, ceramics or polymers. Nanoparticles can either be in their dry state as powders or in dispersions. Colloids are defined as particles, which are dispersed in a continuous medium and they can have a size between 1 nm and 1 μm in at least one dimension.³⁴ Therefore, dispersed nanoparticles are included in the definition of colloids. A more relevant prerequisite of nanoparticles, which makes them highly interesting for applications, is their deviation in physical and chemical properties from the respective bulk counterpart. Nanoparticles exhibit size and shape dependent properties, which can be tuned over a wide range, whereas the properties of bulk material are independent from such influences. Their large surface to volume ratio leads to enormous specific surface areas making them valuable candidates for applications in catalysis. Thus, the application of nanoparticles instead of conventional catalysts could drastically reduce the required material amount. The high surface area may also impact oxidation or digestion in biological experiments/systems.¹⁰⁸ Particularly small nanoparticle crystals (1 - 10 nm) of semiconducting materials, known as quantum dots, exhibit strongly size dependent optical and electronic properties due to exciton confinement in all three dimensions.¹⁰⁹ Consequently, the nanocrystal possesses discrete electronic states and optical transitions (in contrast to the continuous density of states of the bulk).¹¹⁰ Thereby, tuning of the emission wavelength throughout the ultraviolet, visible and near and middle infrared spectrum becomes feasible. Metal nanoparticles also demonstrate exciting optical properties with a size- and shape-dependent absorption.¹¹¹⁻¹¹² Excitation with an electromagnetic wave of the entire particle leads to collective oscillations of the free negatively charged electrons around the bound positively charged core. This effect is known as localized surface plasmons and was discussed in more detail in section 1.1.1. The resonance wavelength is not only sensitive to inherent particle properties but also to the surrounding dielectric environment making it suitable for refractive index sensing applications. High local fields close to the nanoparticles surface also make them valuable candidates to increase the sensitivity of other detection techniques. This effect is for example employed in surface enhanced Raman spectroscopy (SERS).¹¹³⁻¹¹⁴

1.2.1 Top-down vs Bottom-up

Today many methods for the preparation of nanoparticles exist and are chosen depending on the desired final properties and applications. All routes have some advantages and

disadvantages. In general, one can distinguish between top-down and bottom-up approaches. In the first case one starts with the bulk material and uses disruptive forces to break down the material in order to form nanoparticles.¹¹⁵ Typical examples are ball milling techniques¹¹⁶⁻¹²², anodization¹²³⁻¹²⁵ or the more sophisticated method e-beam lithography¹⁰³. Milling techniques are a very cheap and simple method for large-scale nanoparticle production. It allows for tuning of the physical and morphological properties by adjustment of the milling media, speed, atmosphere, duration and the ball to powder weight ratio. Moreover, using wet or dry milling and the type of mill (vibrator mill, attritor mill, tumbler ball mill) define the result.¹¹⁵ However, one drawback lies in the poor control of particle shape and usually broad size distribution.

Bottom-up approaches can be divided into physical and chemical techniques. Physical methods are based on physical vapor deposition (PVD) of a vapor phase species that was generated by evaporation (thermal, e-beam)¹²⁶⁻¹²⁷, sputtering¹²⁸⁻¹²⁹, plasma arching¹³⁰⁻¹³¹ or laser ablation¹³²⁻¹³⁵. Depending on the deposition conditions i.e. high/low vacuum and the present gas type (inert or reactive gasses), nanoparticle formation can take place on a substrate or already in the gas phase. An advantage of PVD methods is the high purity of the synthesized nanoparticles and that the syntheses are rather simple. The obtained particles are usually between 1 – 30 nm, free from solvents and surface coatings. This can be of advantage and suitable for applications like catalysis, where very high surface to volume ratios and pristine surfaces are of utmost importance. At the same time, this can present a major drawback since particles usually tend to aggregate. They may react with their surroundings and cannot be dispersed into solvents for post processing. In addition, larger particles are hard to produce with PVD methods and the shape control is rather poor.

However, the ability of particles to self-assemble into ordered crystals is highly dependent on the interaction between the single particles and a high control over their size, shape, and uniformity is mandatory. Thus, top-down methods and particles prepared by PVD are not well suited for the planned application. A promising approach that can on the one hand yield highly tunable and uniform particle shapes and on the other hand allows control over the particles surface properties is wet-chemical synthesis. Highly monodisperse inorganic colloids can be formed via sol-gel synthesis¹³⁶⁻¹⁴⁵ or the reduction of ionic precursors.¹⁴⁶ Analogously, polymerization methods like (mini/micro) emulsion polymerization, dispersion polymerization, suspension polymerization and precipitation polymerization are used for the preparation of organic colloidal particles.¹⁴⁷⁻¹⁵³ In order to control particle growth processes, which is vital to obtain uniform particles, it is important to have a certain understanding of the underlying

growth mechanism. Therefore, the next chapter will give a basic introduction into nucleation and growth theory.

1.2.2 Nanoparticle Nucleation and Growth

The classical nucleation theory (CNT) was developed by Becker and Döring in the 1930s and describes the condensation of a vapor phase into a liquid phase.¹⁵⁴ Here, it is proposed that a thermodynamic system tends to minimize its Gibbs free energy by maximizing the entropy of the whole system. This theory was then extended to precipitation and crystallization processes of solids. LaMer's theory, proposed in the 1950s, employs the thermodynamic theory for the description of nanoparticle growth processes. First CNT is applied to describe nucleation as a burst nucleation event before a separated particle growth step is introduced.¹⁵⁵⁻¹⁵⁶

A qualitative description of the nucleation and growth process following LaMer's theory is depicted in Figure 1.18 (a) and is divided into three phases:

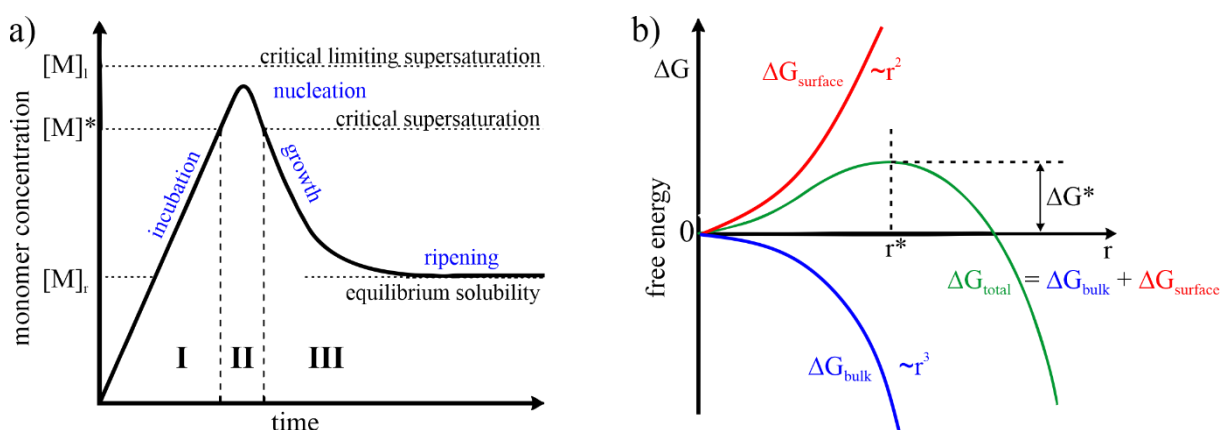


Figure 1.18 (a) Schematic diagram of the nucleation process according to LaMer and Dinegar.¹⁵⁵ The solid black curve qualitatively describes the monomer concentration during incubation (phase I), nucleation above the critical supersaturation (phase II) and the growth and ripening (phase III). (b) Diagram of the free energy ΔG as a function of the nucleus radius r according to the classical nucleation theory based on equation (1.33). The red curve shows the r^2 dependence of the surface free energy term $\Delta G_{\text{surface}}$, the blue curve the r^3 dependence of the negative bulk free energy ΔG_{bulk} of the nucleus. In green the total free energy ΔG_{total} , the sum of the surface and bulk term, is shown together with the critical radius r^* and the critical free energy ΔG^* .

Phase I is the incubation period. Here, the precursor material reacts into the necessary monomer units. For instance, metal salts are reduced into elemental metal atoms, which serve as monomers in a metal nanoparticle synthesis. The monomer concentration $[M]$ increases steadily. When a critical concentration $[M]^*$ is reached, the system enters a metastable state (phase II) and becomes heterogeneous by the onset of nucleation. The fast nucleation process consumes the monomer in the supersaturated state until the concentration has decreased below $[M]^*$. Then, phase III starts with the mere growth of the nanoparticle following for example

diffusion-limited or reaction-limited processes. When the monomer concentration reaches the equilibrium solubility $[M]_b$ slow ripening processes start, which can lead to a slow increase in particle size and potentially narrowing of the size distribution. According to LaMer, a short, well defined nucleation period with a well separated growth step is necessary to obtain a narrow size distribution of the final nanoparticles. However, recent studies suggest that the actual nucleation and growth processes in most systems are much more complex.¹⁵⁷⁻¹⁵⁸ In fact, the phases described above might overlap and can be accompanied by coalescence, oriented attachment, aggregation or intraparticle growth.

In the following, a short introduction in the classical nucleation theory and diffusion-limited as well as surface-reaction-limited growth is given based on review papers by Polte *et al.*¹⁵⁷ and Thanh *et al.*¹⁵⁹

The thermodynamic description of homogeneous nucleation is based on the total free energy of a nanoparticle, which is defined as the sum of the bulk free energy, ΔG_{bulk} , a negative term, and the surface free energy, $\Delta G_{\text{surface}}$, a positive term (compare Figure 1.18 (b)). The bulk term gives the energy of a favorable bonding between a monomer and a cluster that leads to a lowering of the total Gibbs bulk free energy. Opposed to that, the surface term describes the unfavorable effects, which occur due to the formation of a new interface. The total free energy ΔG of a spherical nucleus with the radius r , the surface energy γ and the free energy of the bulk crystal ΔG_v can be determined using equation (1.33).^{157, 159-161}

$$\Delta G = \Delta G_{\text{bulk}} + \Delta G_{\text{surface}} = -\frac{4}{3}\pi r^3 |\Delta G_v| + 4\pi r^2 \gamma \quad (1.33)$$

The free energy of the bulk crystal, ΔG_v , depends on the temperature T , the Boltzmann constant k_B , its molar volume v and the supersaturation of the monomer in solution S according to equation (1.34).¹⁵⁹ S is defined as the ratio of the concentration of the monomer in solution $[M]_b$ and the equilibrium concentration $[M]_\infty$ of the monomer:

$$\Delta G_v = \frac{-k_B T \ln(S)}{v} \quad (1.34)$$

If a system is not supersaturated with monomer ($S < 1$) no crystallization will occur. Additionally, up to the point where the nucleus has reached a critical radius r^* , the nucleus will most probably dissolve again in order to decrease its local free energy. This critical radius can be determined by differentiating ΔG with respect to r :

$$\frac{d\Delta G}{dr} = 0 \quad (1.35)$$

$$r^* = \frac{2 \gamma}{|\Delta G_v|} = \frac{2 \gamma v}{k_B T \ln(S)} \quad (1.36)$$

Substituting r in equation (1.33) with the expression for r^* from equation (1.36) the critical Gibbs free energy ΔG^* can be determined as shown in equation (1.37).

$$\Delta G^* = \frac{16 \pi \gamma^3}{3 |\Delta G_v|^2} = \frac{4}{3} \pi \gamma (r^*)^2 \quad (1.37)$$

From equation (1.36), we can see that the critical radius depends on several experimental parameters. The most straight forward control variable is the temperature T . Moreover, the surface energy γ can be controlled by the addition of stabilizing agents during the synthesis. A very important parameter is the supersaturation S . One can see that a lower supersaturation requires a larger particle radius in order to form stable nuclei. This explains the occurrence of an effect known as Ostwald-ripening: As the synthesis proceeds, monomer is consumed continuously and the supersaturation decreases. At a certain point, r^* is larger than the smallest nuclei, which are then dissolved back into dispersion and serve as monomer during particle growth.

For the description of the nucleation rate of N particles during a time t , an Arrhenius type equation, can be used, with the activation energy ΔG^* and the pre-exponential factor A (equation (1.38)).

$$\frac{dN}{dt} = A \exp\left(-\frac{\Delta G^*}{k_B T}\right) = A \exp\left(+\frac{16 \pi \gamma^3 v^2}{3 k_B^3 T^3 (\ln(S))^2}\right) \quad (1.38)$$

Here, again the rate of nucleation depends on the three experimental parameters surface energy, temperature and supersaturation.

So far, we considered homogeneous nucleation. However, the nuclei are often formed at an already existing surface, especially in the case of seeded-growth synthesis. This globally decreases the energy barrier that has to be overcome. The earliest nuclei formed at the interface no longer have a spherical shape, which is an assumption for classical nucleation theory. Instead, they form rather cap-like structures. If the nucleus and the surface have a high affinity towards each other, low contact angles θ will be created ($\theta < \pi$) and the surface term in the Gibbs free energy equation will be strongly reduced. Therefore, a correction term, which is a function of the contact angle, is multiplied with the critical free energy required for

homogeneous nucleation in order to obtain the critical free energy for heterogeneous nucleation (equation (1.39)).

$$\Delta G_{hetero}^* = \phi \Delta G_{homo}^* \quad (1.39)$$

with

$$\phi = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad (1.40)$$

After nucleation, two processes play an important role in the classical growth model: the monomer's diffusion to the surface of the cluster and the surface reaction itself.¹⁶²

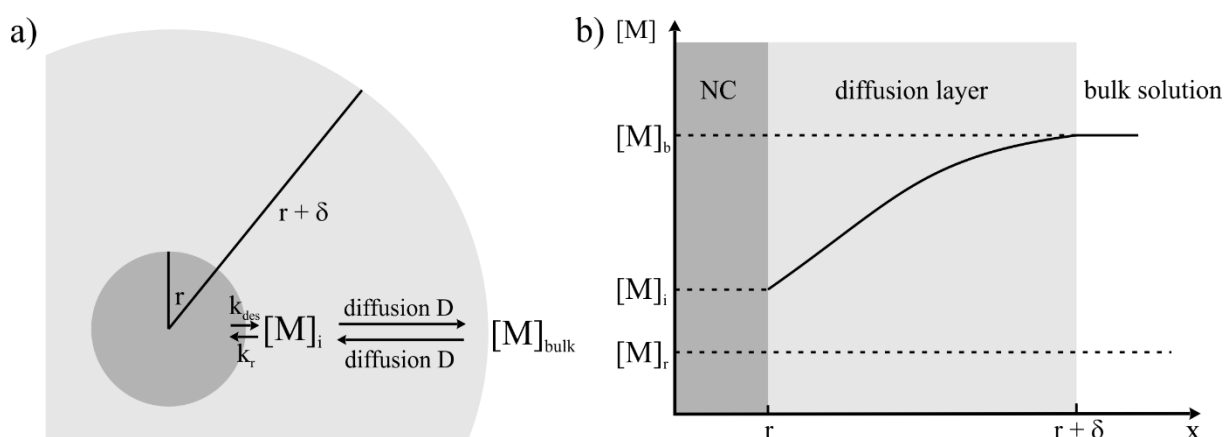


Figure 1.19 (a) Schematic illustration of the diffusion layer around the nanocrystal NC with radius r and diffusion layer δ . $[M]_i$ and $[M]_{bulk}$ are the interfacial and bulk monomer concentrations. Diffusion with the diffusion coefficient D leads to monomer transport within the diffusion layer. The particle growth is controlled by the rate constant k_r and the particle dissolution by k_{des} . (b) Diagram of the monomer concentration $[M]$ in dependence of the distance x from the center of the nanocrystal. $[M]_r$ is the solubility of the particle. (a) Adapted with permission from Ref. ¹⁶³. ©2009 American Chemical Society. (b) Adapted with permission from Ref. ¹⁶⁰. ©2011 WILEY-VCH.

When considering a single nucleus with the radius r several monomer concentrations depending on the distance x can be found as depicted in Figure 1.19. $[M]_b$ is the bulk concentration of the monomer in solution, $[M]_i$ the monomer concentration at the interface and $[M]_r$ the solubility of the particle ($[M]_r = k_{des}/k_r$). The diffusive layer around the particle has the thickness δ . The diffusion coefficient D describes the monomer diffusion towards the nucleus and the reaction rate of the monomer at the particle surface is labelled k . From these considerations the growth reaction can either be diffusion- or reaction-limited and consequently two different growth rates can be derived. If a reaction is purely diffusion-limited, the reaction of the monomer with the surface occurs instantaneously, which means that $[M]_i \approx [M]_r$. On the other hand, if the growth is reaction-limited the concentration of the diffusion layer will be in an equilibrium with the bulk monomer concentration, and $[M]_i \approx [M]_b$. Combining these assumptions and Fick's law,

Sugimoto was the first to derive rate equations for both cases.¹⁶²⁻¹⁶³ The diffusion-limited growth rate in dependence of the radius r and the critical radius r^* can therefore be described by:¹⁵⁹

$$\frac{dr}{dt} = \frac{D}{r} \frac{2 \gamma v^2 [M]_b}{k_B T} \left(\frac{1}{r^*} - \frac{1}{r} \right) \quad (1.41)$$

And the reaction-limited growth rate by:¹⁵⁹

$$\frac{dr}{dt} = k \frac{2 \gamma v^2 [M]_b}{R T} \left(\frac{1}{r^*} - \frac{1}{r} \right) \quad (1.42)$$

For the diffusion-limited case, the reaction rate is shown as function of the particle radius in Figure 1.20 (a). Up to a particle radius of $2r^*$, the size distribution will broaden because larger particles growth faster than smaller ones. After that, the particle growth of the larger particles slows down below the growth rate of smaller particles and thus the size distribution begins to narrow. At late stages of the synthesis, when the supersaturation in the solution decreases, this narrowing will compete with the effects coming from Ostwald-ripening. The effect of Ostwald ripening is shown in Figure 1.20 (b). According to Fick's first law, a diffusion current flowing towards a nanoparticle requires a concentration gradient with decreasing concentration from the bulk towards the nanoparticles surface (compare Figure 1.19 (b)). At the same time, there will always be some diffusion away from the particle surface. As long as this value is smaller than the flow towards the particle, the net diffusion current will lead to a particle growth. If we now consider two differently sized particles we need to take the Gibbs-Thomson equation into account, which describes an additional chemical potential for spherical particles leading to a solubility of the particle $[M]_r$ that depends on r . A schematic depiction is shown in Figure 1.20 (b) at two different reaction times. Small particles with r_1 possess a higher equilibrium solubility $[M]_{r(r_1)}$ than larger particles with r_2 ($[M]_{r(r_2)}$). As long as both particle solubilities lie below the bulk monomer concentration $[M]_{\text{bulk}}$, both particle sizes will continue to grow due to a net diffusional flow towards the interface (top). However, when $[M]_{\text{bulk}}$ decreases due to monomer consumption (decreasing supersaturation), $[M]_{\text{bulk}}$ will eventually be smaller than $[M]_{r(r_1)}$. Now, the net diffusion current flows away from the particle, leading to the dissolution of the small particle whereas the larger particle (r_2) will continue to grow and consume the monomers provided by the dissolving smaller particle.

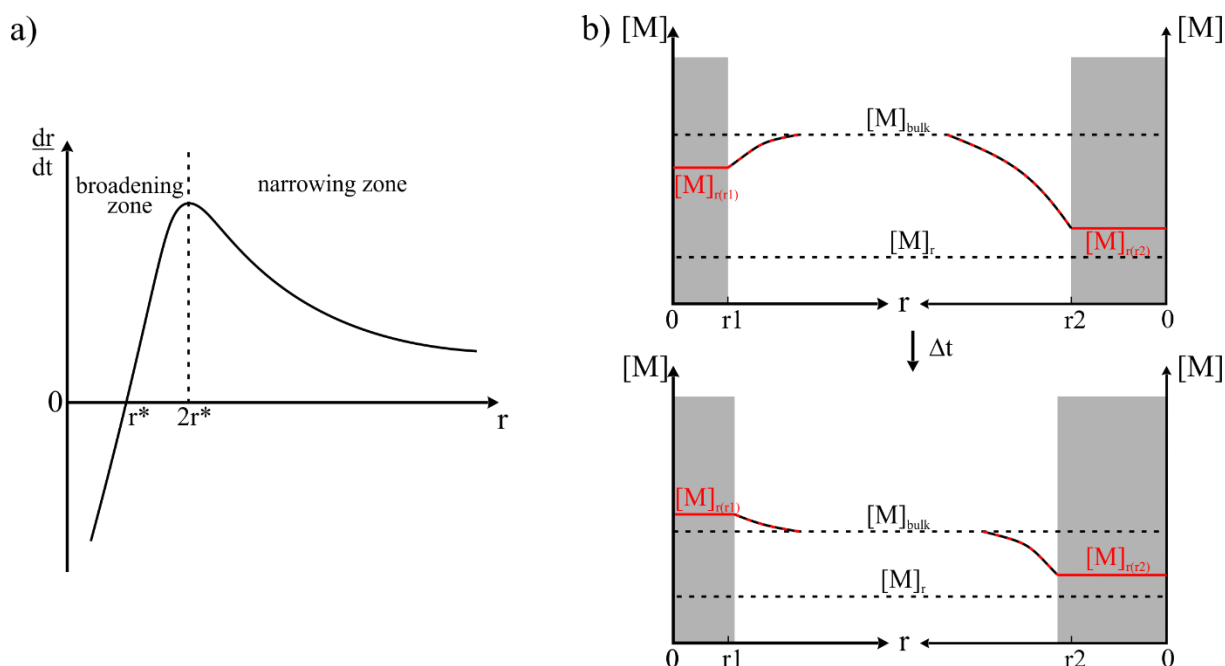


Figure 1.20 (a) Growth rate as function of the particle radius r for a diffusion limited growth indicating the self-broadening and narrowing zone. (b) Solubility of a particle $[M]_r$ in dependence of particle radius r . Top: Net flow of monomer towards the surface of the small $r(r1)$ and the larger particle $r(r2)$ due to higher monomer concentration in bulk $[M]_{\text{bulk}}$ than at the particle surfaces $[M]_{r(r1)}$ and $[M]_{r(r2)}$ leading to particle growth in both cases. Bottom: Ostwald ripening of particle dispersion as reaction proceeds (Δt) and monomer concentration in bulk $[M]_{\text{bulk}}$ decreases; A net flow of monomer away from the smaller particle surface ($[M]_{r(r1)} > [M]_{\text{bulk}}$) leads to dissolution of the small particle, while the larger particle continues to grow as $[M]_{\text{bulk}} > [M]_{r(r2)}$.

1.2.3 Wet-Chemical Metal Nanoparticle Synthesis

The reduction of metal salts is a popular way to prepare (noble) metal nanoparticles by either employing (bio)chemical agents, photochemical or electrochemical methods. In the following, I will introduce concepts and rules for the synthesis of silver and gold nanoparticles. I will show that their shape and size can be influenced with additives like surfactants, ligands, polymers and foreign ions or by the use of hard or soft templates.

One of the most famous and widely used methods to prepare gold nanoparticles of approximately 15 nm is the reduction of HAuCl_4 with citrate following a protocol published by Turkevich and Enustün in 1963.¹⁶⁴ Here, an aqueous solution of the gold precursor is heated until boiling and a hot citrate solution is added under heavy stirring. The citrate serves as reducing agent and stabilizing ligand that attaches to the surface of the nanoparticles via electrostatic interaction forces. In an optimized protocol from Schulz *et al.* the addition is reversed and an additional adjustment of the pH lead to more monodispers particles.¹⁶⁵ By using a silver precursor instead of the gold precursor, spherical silver particles can be synthesized with citrate as reducing agent.¹⁶⁶

For larger particles or anisotropic particle shapes, seeded growth methods are most often used as they provide a higher growth control. Usually the first step is the synthesis of monocrystalline spherical seed particles of approximately 4-5 nm in diameter. In a second step, the seeds are overgrown in a controlled fashion, where facets can be selectively overgrown in order to prepare larger spheres¹⁶⁶⁻¹⁶⁹, rods¹⁷⁰⁻¹⁷⁴, cubes¹⁷⁵⁻¹⁷⁷, platelets¹⁷⁸⁻¹⁷⁹, or other shapes¹⁸⁰⁻¹⁸⁴ by passivation of certain facets. In Figure 1.21, various examples are displayed.

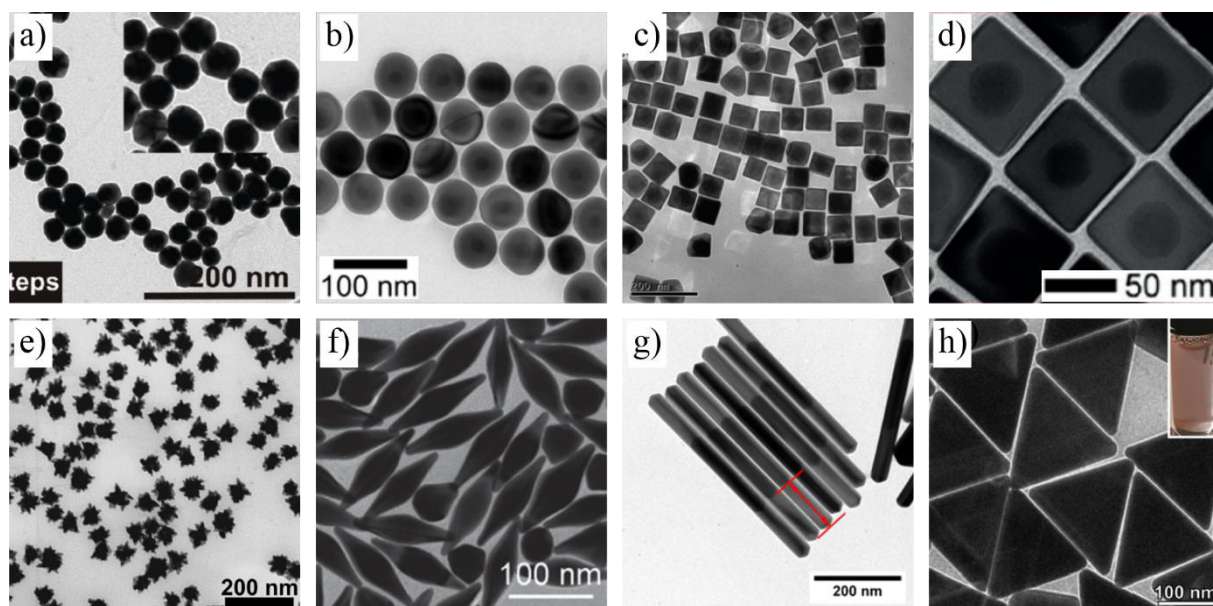


Figure 1.21 TEM images of gold and silver particles of various shapes. (a) Silver nanospheres, (b) bimetallic nanospheres with gold cores and silver shells, (c) bimetallic nanocubes with spherical gold cores and silver shells, (d) bimetallic nanocubes with spherical gold cores, surrounding silver cubes and a thin outer gold protection layer, (e) gold nanostars, (f) bimetallic nanodiamond with gold cores and silver shells, (g) bimetallic nanorods with gold nanorod cores and silver rod ends, (h) gold triangles. (a) Reprinted with permission from Ref. ¹⁶⁷. ©2011 American Chemical Society (b) Reprinted with permission from Ref. ¹⁸⁶. ©2019 American Chemical Society (c) Reprinted with permission from Ref. ¹⁷⁵. ©2012 American Chemical Society (d) Reprinted with permission from Ref. ¹⁷⁷. ©2017 Wiley-VCH (e) Reprinted with permission from Ref. ¹⁸⁴. ©2008 IOP Publishing (f) Reprinted with permission from Ref. ¹⁸². ©2012 The Royal Society of Chemistry (g) Reprinted with permission from Ref. ¹⁷¹. ©2015 American Chemical Society (h) Reprinted with permission from Ref. ¹¹³. ©2018 American Chemical Society.

Bastús *et al.* established a protocol for spherical citrate-stabilized gold¹⁶⁷ and silver¹⁶⁸ particles of up to 200 nm in diameter. A precise control of the size and optical properties is possible employing multiple growth steps. Silver plates of different shapes were synthesized by Jiang in 2006¹⁷⁸ and triangular gold platelets by Sajanalal in 2008¹⁸⁵ using an electrical potential assisted seeded growth method. Highly monodisperse spherical Au nanoparticles were synthesized by Steiner *et al.* using CTAB (Cetyltrimethylammoniumbromide) capped 2 nm Wulff seeds which were overgrown to 8 nm CTAC (Cetyltrimethylammoniumchloride) capped seed particles in a

one shot synthesis.¹⁶⁹ Further overgrowth yielded highly spherical nanoparticles of 70 nm in diameter with a narrow size distribution.¹⁶⁹ Based on the same kind of particles also silver nanocubes with a thin protective Au coating were obtained by careful selection of reactant ratios and added ions.¹⁷⁷

The potential to use polyols or alcohols as reducing agents at elevated temperature was demonstrated for various reaction conditions and resultant particle shapes. Ag nano-hexapods were synthesized by using ethylene glycol as reducing agent and solvent for AgNO₃ and PVP as stabilizing agent.¹⁸⁷ Another way to obtain anisotropic particle shapes, is to use a template structure. Ag spheres, rods and wires were prepared on the surface of a DNA network¹⁸⁸ and a water/PVP/n-pentanol system was used for the controlled synthesis of Au nanostructures¹⁸⁹. Electrochemical synthesis was employed for the synthesis of Ag nanowires between the electrodes while liquid crystals supported the growth in the selected direction.¹⁹⁰ Other popular templates are for example track-etched polymers and anodized aluminum oxide for the synthesis of Au nanorods with multipole resonances.¹⁹¹ Also photochemical reactions can be used to initiate the reduction of precursor in order to form triangular shaped Ag nanoparticles¹⁹², as well as platelike triangular, hexagonally shaped or ellipsoidally shaped Au nanoparticles depending on the precursor and stabilizing agent concentration.¹⁹³ Also a combination of photochemical reduction assisted by a reducing agent can be used to synthesize Au rods.¹⁹⁴

Biosynthesis is another possibility to produce noble metal nanoparticles. It is an environmentally friendly and usually cost efficient method but typically produces spherical shapes with a wide size distribution and a mixture of shapes. Au nanoparticles in a plant were prepared by Gardea *et al.*¹⁹⁵ Au nanoprisms (with a high percentage of triangles) were synthesized with a lemongrass plant extract¹⁹⁶ which reduces HAuCl₄ and Au triangles and Ag nanoparticles using an aloe vera plant extract¹⁹⁷. Bioreduction of AuCl₄⁻ ions by the Fungus *Verticillium* sp. and surface trapping of the formed Au nanoparticles was shown by Mukherjee.¹⁹⁸

The size and shape of the particles formed by all presented reducing methods generally depend on the selected reducing agent, surfactants and concentrations. Careful variation of these factors enables the controlled synthesis of Au nanoparticles with different shapes.¹⁹⁹ In a Pt nanoparticle growth protocol with H₂ as reducing agent and sodium polyacrylate as capping agent, changes in synthesis composition ratios resulted in the tunability of the ratio of different shapes.²⁰⁰ Additionally, ions, polymers and impurities can influence the ability to form nanoparticles and the morphology. They can selectively bind to certain surface facets of the

nanocrystal and either promote or inhibit the growth along a certain axis. Also, the seed particles should ideally be monocrystalline. When polycrystalline seeds are used this may result in a completely uncontrolled mixture of particle sizes and shapes.

Unwanted ions might also lead to the formation of unreactive precipitates that hinder further nanoparticle growth. In a controlled fashion, added ions can help to shape the final product. In a polyol synthesis of Ag nanocubes, where ethylene glycol served as solvent and reducing agent, added sulfide promotes the cubic shape and PVP selectively binds to [100] Ag facets further facilitating the formation of the cubic shape.²⁰¹ An iodine contaminant in CTAB, a surfactant that can be used for the synthesis of Au nanorods, was found to be a key shape-determining element since it selectively binds to the [111] Au facet and thereby promotes anisotropic particle growth.²⁰² When starting with seed particles, pure CTAB and adjusting the iodine concentration three target morphologies (large spheres, rods and nanoprisms) can be obtained by controlled seed-mediated growth.¹⁷⁹

1.2.4 Metal-Hydrogel Core-Shell Nanoparticles

In order to stabilize nanoparticles against aggregation and provide them with a tunable spacer for the 2D assembly, the metal nanoparticle can be encapsulated into a polymer shell via precipitation polymerization.¹⁵³ In this type of synthesis, the monomers and the initiator are soluble in the solvent and the reaction generally occurs by a homogeneous nucleation mechanism. After a certain molecular weight is achieved, the oligomer/polymer becomes insoluble in the former solvent and starts to precipitate leading to particle growth. Adjustment of the reaction parameters enables the formation of very monodisperse nanoparticles, which can also be cross-linked in the course of polymerization.

Since Pelton and Chibante showed the first precipitation polymerization of PNIPAM in 1986²⁰³, this method is widely used in aqueous media for the synthesis of microgel particles from the monomers *N*-isopropylacrylamide²⁰³⁻²¹³ and *N*-vinylcaprolactam²¹⁴⁻²¹⁵. Both monomers are of particular interest owing to their resulting homopolymer responsiveness to temperature or pH changes. Due to the mono-functionality of these monomers, a cross-linker molecule like BIS (*N,N'*-methylene bisacrylamide), EGDMA (ethylene glycol dimethacrylate) or TEGDMA (triethylene glycol dimethacrylate) is required in order to form stable particles.

In general, microgels are usually spherical particles between 50 nm and 10 μ m and form stable dispersions in a continuous medium.²¹⁶ They can be characterized by their average crosslink-density and degree of swelling with solvent, which depends on the prevailing polymer-polymer and polymer-solvent interactions. These interactions can be influenced by the surrounding

temperature, pH and ionic strength.²¹⁶⁻²¹⁹ PNIPAM microgel particles for instance exhibit a volume phase transition temperature (VPTT) close to the lower critical solution temperature (LCST) of the non-cross-linked PNIPAM chains in water.²²⁰ Above a critical temperature the collapse of the polymer network leads to a phase separation.²²¹⁻²²² The exact interactions leading to the phase separation are complex.

The amide side-chains form hydrogen bonds with the water molecules building polymer-water interactions. At the same time, the isopropyl groups exhibit an affinity towards one another because of their incompatibility with water.²²² If the temperature is increased above the VPTT, the endothermic release of water molecules from the polymer network leads to an entropy increase in the water-polymer system, dominating polymer-polymer interactions and consequently to a coil-to-globule transition of the polymer chains.²²³⁻²²⁷

This behavior is also exploited in the synthesis of PNIPAM microgel particles. As the precipitation polymerization is usually conducted at elevated temperature (50-70 °C), i.e. above the LCST (32 °C), the growing polymer chain becomes insoluble in water when the oligomer radicals reach a certain molecular weight. The coil-to-globule transition takes place and precursor particles are formed. These particles growth into larger particles due to the aggregation of multiple precursor particles, deposition of the precursor particles onto an existing (polymer) particle or by further monomer addition onto the macroradicals. Due to the incorporation of the initiator fragments (bearing for example sulfate groups) into the polymer chains during the nucleation and growth process the particles become stabilized by electrostatic repulsion. In contrast to emulsion polymerization techniques, where the reaction of the water-insoluble monomer (e.g. styrene, methyl methacrylate (MMA)) is conducted in monomer swollen micelles, there is still a lot of residual water (approximately 30 %) left in the polymer network.²¹¹ This leads to a much less compact particle structure as one can see in the cryo-SEM image depicted in Figure 1.22 (a). Once the reaction is completed and the dispersion is cooled below the VPTT, the particles swell with water and develop a hairy morphology. The stability and degree of swelling of the final microgel particles depends on the degree of cross-linking during the synthesis (compare Figure 1.22 (b)).

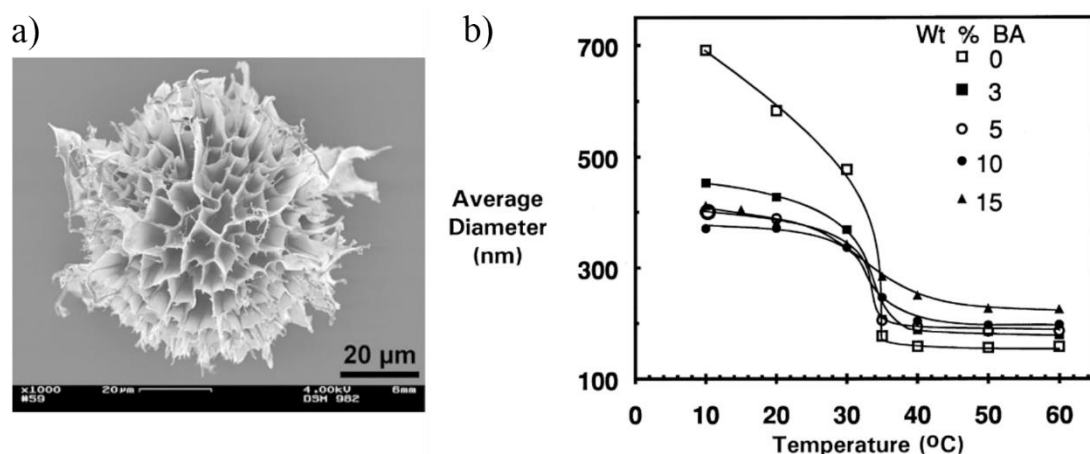


Figure 1.22 (a) Cryo-SEM image of a PNIPAM microgel particle. (b) Swelling curves of PNIPAM microgel particles in water with increasing cross-linker concentration (BA = methylene bisacrylamide). (a) Reprinted with permission from Ref. ²¹⁶. ©2010 Springer-Verlag Berlin (b) Reprinted with permission from Ref. ²¹¹. ©2000 Elsevier Science B.V.

During the polymerization process of aqueous microgels different co-monomers²²⁸⁻²³⁰ and macromonomers²³¹⁻²³⁴ can be incorporated into the microgel network, which allows for tuning the particle properties like temperature- and pH-response, size and density.

Furthermore, hybrid particles can be prepared by encapsulating nanoparticles as cores during the synthesis. Here, for example differently composed polymer nanoparticles²³⁵⁻²³⁸, silica particles²³⁹⁻²⁴³ or metal nanoparticles²⁴⁴⁻²⁴⁹ can be used. Initially, metal cores had to be encapsulated into thin silica or polystyrene shells in order to enable encapsulation with PNIPAM shells²⁴⁶, but in 2011 Karg *et al.* introduced a protocol for the incorporation of small, surface-functionalized gold nanoparticles directly into PNIPAM shells.²⁴⁹ Müller *et al.* expanded this protocol to silver nanoparticles.²⁵⁰ The influence of functionalizer and seed concentration was closely investigated by Rauh *et al.* in 2015.²⁵¹ The growth mechanism of the seeded precipitation polymerization is depicted in Figure 1.23 (a). As a starting point, a mixture of monomer, initiator and gold nanoparticles in water is prepared (1). By initiation, negatively charged initiator radicals are formed (2) and the oligomer growth is started. Thereby, a mixture of Au nanoparticles, monomer and oligomer radicals forms (3) and phase separation and the growth of the polymer radicals take place (4). In a last step, the polymer radicals further grow and precipitate onto the Au nanoparticle seeds, forming stable and monodisperse Au-PNIPAM core/shell particles. In (b), a representative TEM image shows the Au cores as black dots surrounded by a grey corona, which is the PNIPAM shell. The contrast originates from the different electron densities of the metallic core and the organic polymer shell. In this example, the nanoparticle concentration was 2.8 nmol/L, a concentration where almost every core is encapsulated into a shell and vice versa. Within a certain window, the shell thickness can be

tuned by variation of the added seed concentration. Below and above that window shells without a core are formed or cores remain without encapsulation, respectively.²⁵¹ The shell (thickness) also influences the optical response of the nanoparticle dispersion (Figure 1.23 (c)). When no nanoparticle seeds are employed (solid black curve), no distinct spectral features are observed. Only a continuous increase in absorbance towards lower wavelengths is visible due to light scattering (Rayleigh-Debye-Gans scattering) caused by the microgel particles.²⁴⁹ Adding gold seeds to the synthesis leads to the formation of a peak at approximately 525 nm, attributed to the LSPR of the gold nanoparticles. As the gold concentration increases, the peak intensity increases as well. At the same time, the scattering contribution from the microgel shell decreases as the microgel shells become thinner and, therefore, scatter light less efficiently. In comparison to a pure Au nanoparticle seed dispersion the LSPR is red-shifted from 518 nm to 525 nm in the encapsulated case due to the increased refractive index environment.²⁴⁹

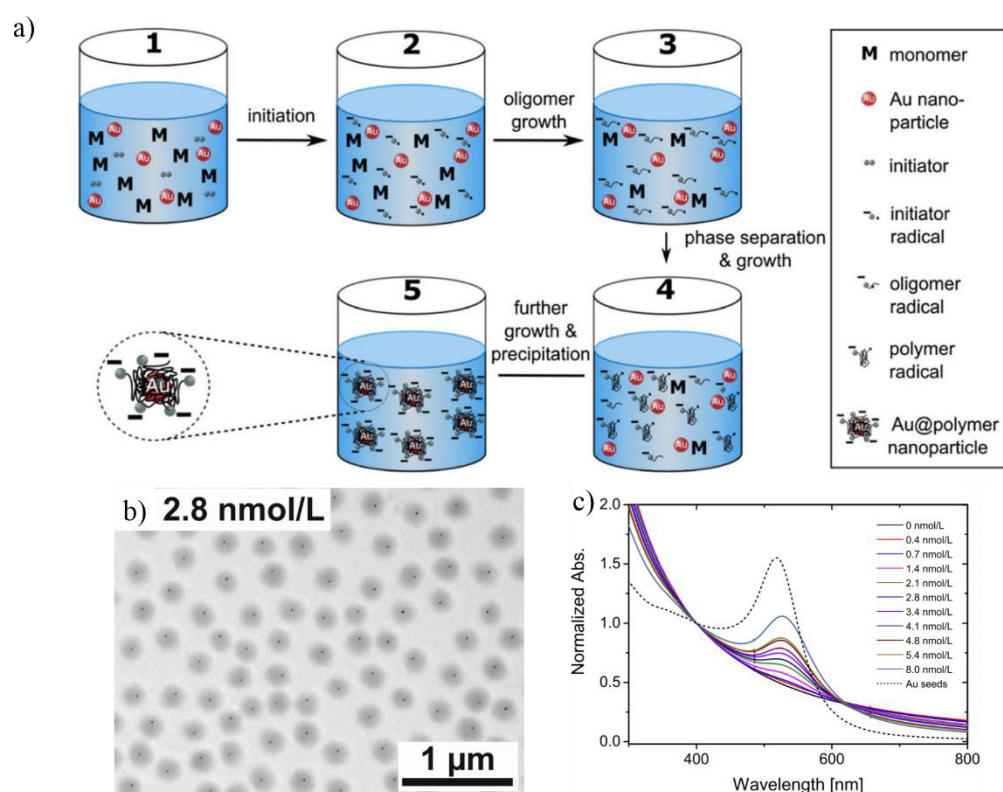
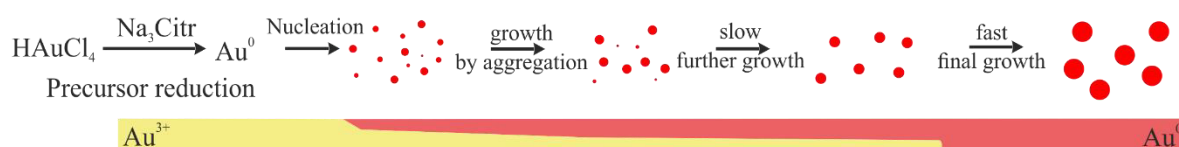


Figure 1.23 Synthesis of Au-PNIPAM core/shell particles via seeded precipitation polymerization. (a) Sketch of growth mechanism. (b) TEM image of final Au-PNIPAM particles using 2.8 nmol/L of 15 nm Au nanoparticle seeds. (c) UV-vis absorbance spectra of only Au seeds (black dotted trace), pure PNIPAM microgel (black trace) and certain mixture ratios leading to the formation of core/shell particles with different shell thicknesses. The spectra are normalized at 400 nm. Adapted with permission from Ref. ²⁵¹ ©2016 Springer Nature.

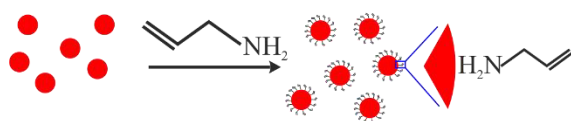
Such Au-PNIPAM particles formed by seeded precipitation polymerization were also employed as building blocks for periodic lattices in this thesis. A schematic description of the

synthesis is depicted in Figure 1.24. First, spherical Au nanoparticles of approximately 12 nm in diameter were prepared following the Turkevich method introduced in the previous chapter (a).¹⁶⁴ Then, as shown in (b), the surface of the particles was functionalized with butenylamine. Next, the functionalized particles were used as seeds in the above introduced seeded-precipitation reaction of the monomer NIPAM (c).²⁵¹ For the cross-linking of the microgels, BIS (*N,N'*-methylenebisacrylamide) was employed. The microgel shells serve a dual purpose. Firstly, steric repulsion stabilizes the plasmonic nanoparticles against aggregation. Secondly, the shell serves as dynamic spacer for the particle arrangement into a regular lattice via self-assembly at the air/water interface. In a last step (d), the encapsulated plasmonic cores were selectively overgrown with gold or silver in order to enhance and tune the optical properties of the small gold cores.

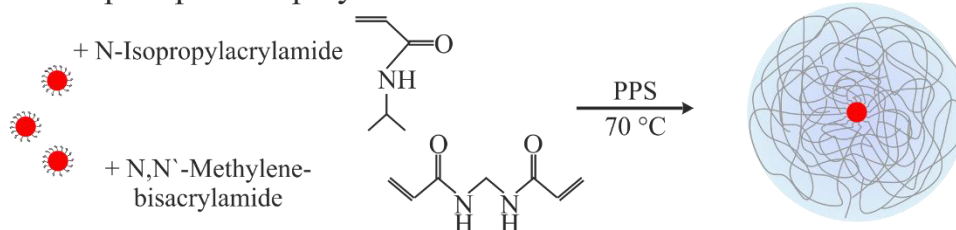
a) Turkevich synthesis



b) Surface functionalization



c) Seeded-precipitation polymerization of PNIPAM



d) Overgrowth of Au core

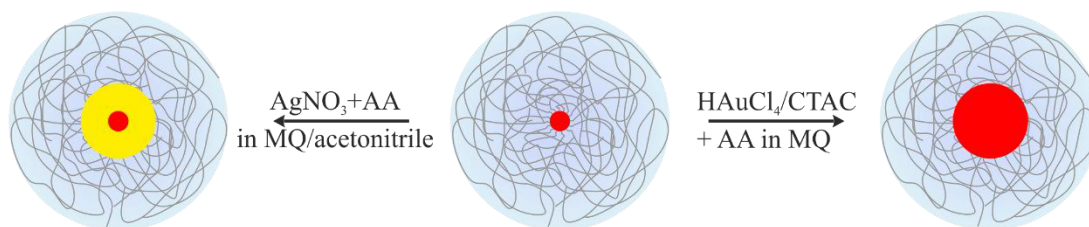


Figure 1.24 Schematic description of the particle synthesis used in this thesis. (a) Synthesis of 12 nm gold nanoparticles according to Turkevich. (b) Gold surface functionalization with butenylamine. (c) Seeded-precipitation polymerization of PNIPAM and BIS initiated with PPS (potassium peroxodisulfate). (d) Overgrowth of encapsulated gold core with silver or gold.

The overgrowth procedures were optimized for our particle systems based on studies by Contreras-Càceres.^{245, 252} For large gold cores of approximately 100 nm in diameter, a seeded growth protocol from Honold *et al.* using ascorbic acid as reducing agent and CTAC as surfactant was used.²⁵³ The two protocols for the overgrowth with silver were developed during this thesis. Initially, a protocol using ascorbic acid as reducing agent and CTAB as surfactant in an aqueous dispersion adapted from Contreras-Càceres *et al.* was used.²⁵⁴ Later, the synthesis was carried out in a water-acetonitrile mixture with ascorbic acid as reducing agent.²⁵⁵ The synthesis in the water-acetonitrile mixture was found to be more reproducible because no CTAB is necessary for the synthesis. Impurities in CTAB that change from dealer to dealer and even from batch to batch made the synthesis using CTAB unpredictable.²⁰²

1.3 Self-Assembly into Colloidal Crystals

In order to understand and control assembly processes it is important to know the different forces that act upon a colloidal system. First, we look at the colloidal stability of particles in dispersions since a stable colloidal dispersion is usually the starting point for a successful, defect-free crystal formation. In a dispersing medium, pristine nanoparticles are unstable and tend to agglomerate due to short-range, attractive van-der-Waals, electrostatic and magnetic forces.¹⁵⁷ Therefore, in order to obtain a stable dispersion, counteracting repulsive forces are required. Usually, these are either obtained by electrostatic Coulomb forces in charged particle systems due to dissociated functional groups or adsorbed ions³⁴ and/or by steric stabilization with either adsorbed or chemically attached large polymeric chains or ligands.²⁵⁶⁻²⁵⁹

1.3.1 Colloidal Stability: Competing Forces in Bulk

When particles are electrostatically stabilized, the surface charge will attract counter-ions and thereby cause solvated ions to form an electric double layer around them. Helmholtz first described this effect for flat surfaces, where the surface is neutralized directly by one bound layer of counter-ions like in plate capacitors. Gouy and Chapman took the thermal motion of ions, which drives them away from the surface, into account and thereby expanded this model. Consequently, a diffuse layer, instead of a well-defined molecular layer, is used to describe the particle-solute interface. The electric potential ψ near a charged surface highly depends on the distance x to the surface and can be described by the Poisson-Boltzmann equation. Finally, the Debye-Hückel approximation (linear term of the general Poisson-Boltzmann equation) allows the description of the potential around a sphere for which the general solution is:³⁴

$$\psi(x) = C_1 e^{-\kappa x} + C_2 e^{\kappa x} \quad (1.43)$$

With

$$\kappa = \sqrt{\frac{2c_0 e^2}{\varepsilon \varepsilon_0 k_B T}} \quad (1.44)$$

κ is the Debye constant, c_0 the bulk salt concentration, ε_0 the vacuum permittivity, ε the relative permittivity, and k_B the Boltzmann constant. C_1 and C_2 are constants, determined by the boundary conditions: Directly at the surface, the potential is equal to the surface potential. At large distances the potential is 0. Consequently, $C_1 = \psi_0$ and $C_2 = 0$ and therefore the potential decreases exponentially:³⁴

$$\psi(x) = \psi_0 e^{-\kappa x} \quad (1.45)$$

The distance where the potential has decayed to $1/e$ of the surface potential is called the Debye length ($\lambda_D = \kappa^{-1}$) and decreases with increasing salt concentration due to more efficient screening of the surface charge at higher concentrations. For monovalent salts in water at 25 °C the Debye length for example is:³⁴

$$\lambda_D = \frac{3.04 \text{ \AA}}{\sqrt{c_0 \frac{L}{mol}}} \quad (1.46)$$

Most importantly, the Debye length gives the length scale of the electrostatic repulsion and describes how an increase in ionic strength can decrease the electrostatic stabilization of a colloidal dispersion.

In order to describe colloidal stability quantitatively, the interplay between electrostatic repulsion and van-der-Waals attraction was employed by Derjaguin, Landau, Verwey, and Overbeek to describe a distance dependent interaction potential U .²⁶⁰⁻²⁶¹ Today, this concept is known as DLVO theory (Figure 1.25 (a)) and is one of the fundamental concepts in colloid chemistry. Depending on the distance d between two particles a net attractive or net repulsive interaction potential U is obtained by summation of the electrostatic (Ψ) and van-der-Waals (U_{vdW}) forces. As depicted in Figure 1.25 a first global minimum at small interparticle distances (I), where irreversible aggregation takes place, and a local minimum at large interparticle distances (III), describing reversible flocculation, occurs due to dominating van-der-Waals forces. In region (II), at intermediate interparticle distances, the repulsive electrostatic interactions are strongest and the height of this energy barrier determines the stability of the dispersion.

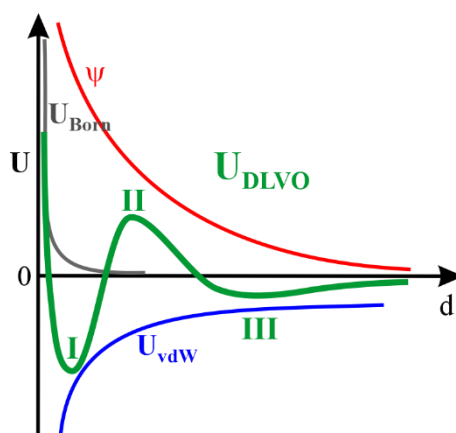


Figure 1.25 Forces acting on colloids in dispersion considered in the DLVO theory and the resulting potential U in dependence of the interparticle distance d . Adapted with permission from Ref. ²⁶² ©2012 The Royal Society of Chemistry.

Additional to electrostatic repulsion, steric repulsion plays an important role in the stabilization of colloidal dispersions. Two effects cause steric stabilization of colloidal particles with a solvated polymer corona. First, steric repulsion occurs due to a loss of entropy when the polymer chains overlap. The compression of the chains limits their mobility. Second, an osmotic pressure difference occurs in the region where the polymer chains overlap, due to a local increase in polymer concentration. This results in a solvent flow towards this region to dilute this locally increased polymer concentration and thereby prevents aggregation.²⁶³⁻²⁶⁴ On the other hand attractive forces between dispersed colloids and dissolved polymer chains can also lead to flocculation of the particles due to bridging, when more than one particle interacts with an individual polymer chain.²⁶⁵ Similarly, additional solutes, such as individually dissolved polymer chains or smaller nanoparticles can lead to depletion flocculation if they do not adsorb to the colloid surface: around the colloidal particles a depletion zone is generated, where no solute is present due to entropic reasons. When two colloids get closer together than the depletion zone, an osmotic pressure difference will occur between the area in-between the particles and the bulk where an increased solute concentration is present. Consequently, a convective flow of the solvent towards the polymer/small particle region will take place and thereby drive the larger colloids towards each other and result in depletion flocculation.²⁶⁵⁻²⁶⁶

Finally, the colloidal stability can be influenced by external forces. In particular, for larger particles, gravitational forces cannot be neglected and can eventually lead to sedimentation. When sedimentation occurs in monodisperse particle systems three-dimensional colloidal crystals can be obtained.²⁶⁷⁻²⁷⁰ The stability/movement of charged particles can also be influenced by electrostatic attraction or the application of an electrophoretic current. In the first case, an oppositely charged substrate is immersed into the colloidal dispersion and random

sequential adsorption will lead to disordered particle monolayers with a low surface coverage.²⁷¹⁻²⁷² For the second process, a direct or alternating current is applied to an electrically conductive substrate while immersed into the dispersion. Again, ordered particle monolayers can be obtained.²⁷³⁻²⁷⁴

1.3.2 Competing Forces at Interfaces

Once colloidal particles are placed at an interface between two phases (gas/liquid or liquid/liquid) additional forces need to be considered. The interface will strongly influence the total interaction potential of the system. First of all, colloidal particles inherently attach to interfaces because an emerging energy minimum efficiently traps the colloid at a fixed position at the interface.²⁷⁵ For example, as everybody knows from daily life oil and water are immiscible and phase separate. Due to the less favorable energy state of the molecules at the interface, the system tries to minimize the interfacial area. When colloids are brought in between the two media, new, energetically favorable water/particle and oil/particle interfaces are formed replacing the original oil/water interface. According to Pieranski, the reduction of the total interfacial energy between a liquid/liquid(gas) interface as well as the increased contact area of the particles with both phases leads to energetic particle trapping at the interface.^{34, 276} For particles with dimensions larger than a few tens of nanometers this adsorption is typically irreversible.²⁷⁵ This behavior is also employed for the stabilization of Pickering emulsions.²⁷⁷ The position of the particle at the interface depends on its wetting properties, size, weight, density and deformability.

The wetting properties depend on the surface chemistry of the particle and determine the vertical particle position in respect to the interface when a particle is adsorbed. For the characterization of this position, the contact angle θ_c can be used. The three possible scenarios are shown in Figure 1.26. Hydrophilic particles form a contact angle θ_c below 90° in respect to the water phase and are mainly immersed into the aqueous phase (a). Hydrophobic particles form a contact angle θ_c larger than 90° and therefore the majority of the particle volume is located in the air or oil phase, respectively (c). In the intermediate case (b) where $\theta_c = 90^\circ$, the affinity towards both phases is the same and the particle sits exactly at the interface.

When multiple particles are adsorbed to an interface, capillary forces between the colloids originating from the deformation of the interface due to the particle wettability have to be considered.²⁷⁸ These capillary forces can be subdivided into immersion forces and flotation forces.²⁷⁹⁻²⁸⁰

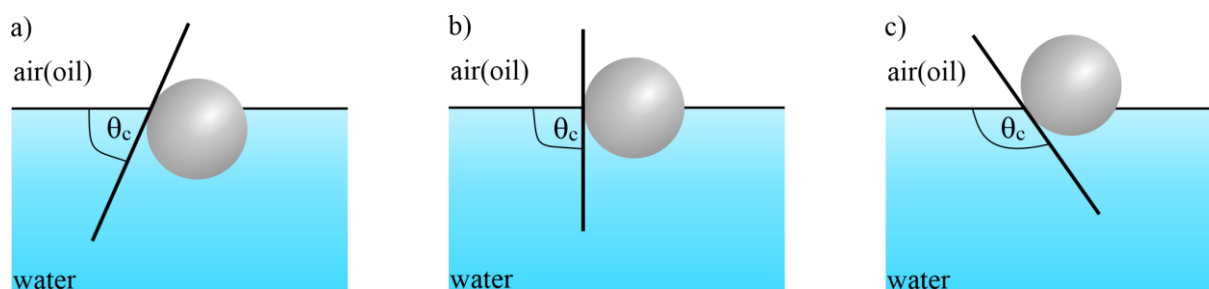


Figure 1.26 Schematic description of the wettability of a hard colloid at an air (oil)/water interface using the contact angle θ_c . (a) Hydrophilic particle with $\theta_c < 90^\circ$. (b) No preference leads to $\theta_c = 90^\circ$. (c) Hydrophobic particle with $\theta_c > 90^\circ$.

Flotation forces occur for large particles at air/water interfaces and are an effect driven by gravity. Buoyancy and gravitational forces deform the interface while not changing the local contact angle θ_c defined by the wettability. For particles with similar wettability, the capillary forces are attractive because of a symmetrical deformation of the interface (compare Figure 1.25 (a)). The Laplace pressure leads to an attraction of the particles in order to minimize the curvature of the interface between the particles. An asymmetrical deformation of the interface due to dissimilar wettability on the other hand leads to a repulsive force. However, for hard particles that possess a diameter smaller than 10 – 20 μm flotation forces disappear.

Immersion forces occur even for smaller particles down to a diameter of 20 nm, when a substrate is coated with a thin liquid film, which is thinner than the particle diameter. This forces the interface to deform according to the wetting properties of the particles. Again, a long range attractive force develop if the particles exhibit similar wettability.

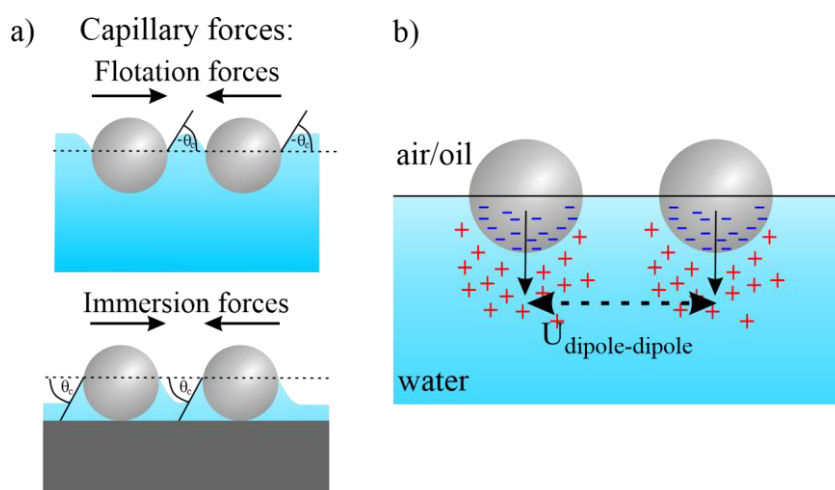


Figure 1.27 Forces acting on colloids at an interface. (a) Capillary Forces: Flotation forces acting at an interface (top) and immersion (bottom) acting on particles sitting at an interface immersed in a thin liquid film. (b) Repulsive dipole force due to symmetric dissociation of ionic groups on the surface of particles trapped at an interface. Adapted with permission from Ref. ²⁶² ©2012 The Royal Society of Chemistry.

Moreover, for particles trapped at an air(oil)/water interface, partial ionic dissociation of ionic groups will lead to an asymmetric charge distribution around the particle due the different polarity of the two phases (Figure 1.25 (b)). This results in parallel oriented dipole moments perpendicular to the surface and therefore additional strong repulsive dipole-dipole forces.^{262,}

281

Similar to the situation in bulk, the competing forces at an interface add up to a total interaction potential, which determines the most likely configuration at the interface. At a low surface coverage, the particles laterally move independent from each other. When the particles approach each other, emerging capillary forces drive the particles together forming aggregates. Depending on the strength of the counteracting electrostatic repulsion due to asymmetric charge distribution the aggregation will either be fast and consequently in an uncontrolled manner or slow and lead to a regular monolayer with a low defect density.²⁸² When highly charged particles are employed, even non-close packed monolayers can be formed outweighing the usually dominating capillary forces. This is especially seen in oil/water interface systems due to prevailing, significantly stronger repulsive forces and lowered capillary attraction.²⁸¹⁻²⁸³ In Figure 1.28, the electrostatic repulsion is altered by trapping the particles either at an air/water (a, d) or at an octane/water (b, e) interface.

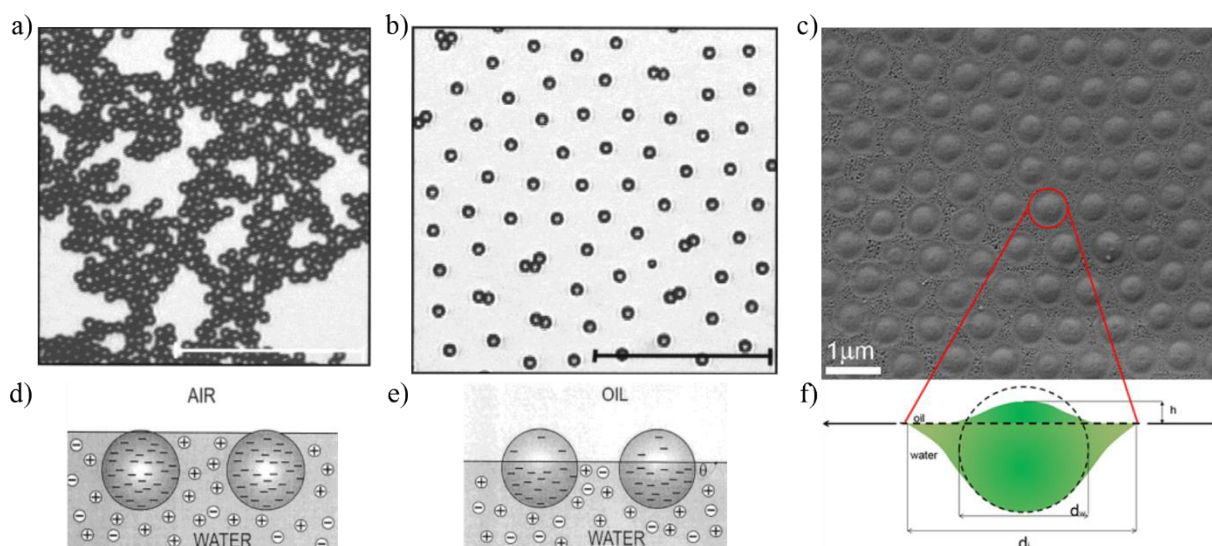


Figure 1.28 Comparison of the structure of particle monolayers in dependence of the particle type and interface. In (a) and (b) 2.6 μm diameter latex particles are at an interface with water (1M NaCl) and air or octane, respectively. In (c) 400 nm diameter PNIPAM-co- methacrylic acid (MAA) hydrogel particles are at an interface of water and heptane. (d) to (f) Sketches illustrating the position of the particles at the interfaces described in (a) to (c). (a, b, d, e,) Reprinted with permission from Ref. ²⁸². ©2000 American Chemical Society. (c,f) Reprinted with permission from Ref. ²⁸⁴. ©2012 American Chemical Society.

In the case of an air/water interface the latex particles are almost fully submerged into the aqueous phase and a mostly homogeneous charge distribution around the particles can occur. Consequently, the dipol-dipol repulsion is low and particle aggregation occurs in a fast and uncontrolled manner. In the second case, where the interface is formed with an octane phase, a significant portion of the particle sits in the hydrophobic phase resulting in a higher asymmetry in charge separation. The dominating dipole-dipole repulsion leads to the formation of a fairly regular hexagonal particle arrangement with large interparticle distances.

When soft, deformable microgel particles or core/shell particles with a microgel shell are considered, additional effects will influence the particle arrangement/behavior at air/liquid or liquid/liquid interfaces. Dispersed at the interface, they spread and deform into a fried-egg like morphology (compare Figure 1.28 (c), (f)) in order to minimize the interfacial area of the two phases as much as possible.²⁸⁵⁻²⁹⁰ At low surface coverages, this deformation is as large as possible because the energy gain due to interface minimization is larger than the energy required for polymer shell deformation. Once the surface coverage is increased, the deformation is reduced and hence the elastic energy is also reduced while the two-phase contact line is still covered by microgel.²⁹¹ Additionally, interpenetration of the hydrogel shells can take place upon compression.²⁹⁰ Moreover, the capillary forces are stronger as compared to hard colloids of similar size due to a larger wetting radius and the extremely rough particle surface.²⁹²⁻²⁹³ Especially for hard-core/soft-shell particles this attraction can lead to the formation of microgel particle islands, even when the interface is not yet covered entirely.^{254, 290, 294-295}

An analytical solution for hard-core/soft-shell particles at liquid-liquid interfaces was presented recently by Vasudevan *et al.*²⁸⁸ They used a free energy model for the prediction of the equilibrium position of a deformable hard-core/soft-shell nanoparticle (CSNP – notation used in reference) at an oil/water interface in dependence of geometrical and compositional properties in the aqueous bulk phase (Compare Figure 1.29). It considers a cross-linked polymer shell for which water is the better solvent in comparison to oil. For the determination of the total free energy F_{total} four contributions are taken into account: (1) The free energy of the shell exposed to the water F_w or (2) the oil phase F_o , respectively, by taking into account the Flory-Huggins theory, (3) The elastic energy penalty $F_{e,i}$ due to stretching of the shell at the interface, and finally, (4) the energy gain F_γ due to the removal of the oil/water interface, where the particle sits. It was found that the CSNP size at the interface strongly depends on the core size and the shell thickness. These two parameters determine the equilibrium position of the core with respect to the interface, which corresponds to the minimum of F_{total} .

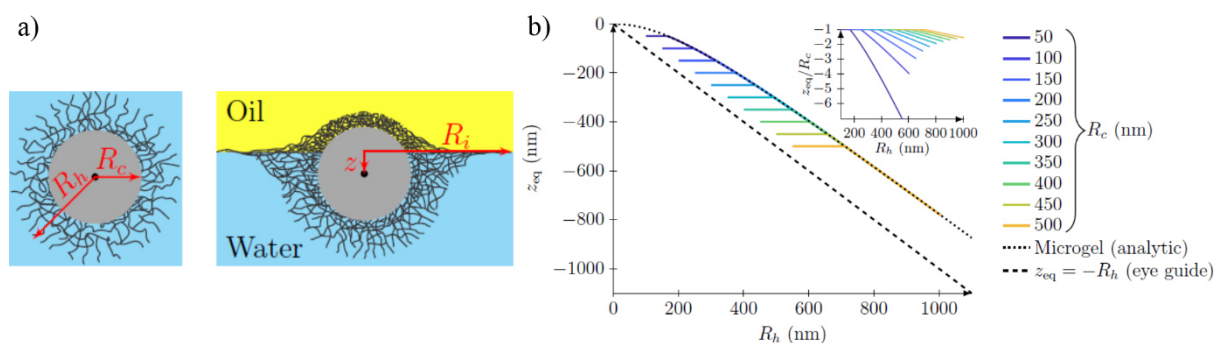


Figure 1.29 Description of a hard-core/soft-shell particle at oil/water interface. (a) Particle sketch at the oil/water interface. (b) Equilibrium distance of the core z_{eq} from the interface obtained from the free-energy minimization model as a function of the hydrodynamic radius R_h in water. The dotted line corresponds to the equilibrium position of a pure microgel. Inset: z_{eq} scaled by R_c as function of R_h . Reprinted with permission from Ref. ²⁸⁸. ©2018 American Chemical Society

For shell thicknesses below a critical value the core just touches the interface ($R_c = z_{eq}$), while being immersed in the aqueous phase (compare sketch in Figure 1.30). This corresponds to a minimum of the F_γ term, where the CSNP covers the maximum area at the interface. In this region the elastic energy penalty $F_{e,i}$ hardly plays any role in comparison to the other contributions. As the shell size is increased beyond a critical value the core detaches from the interface and sits deeper in the aqueous phase. z_{eq} is not determined by F_γ but by the energetic gain from the microgel in the aqueous phase F_w . Consequently, the CSNP behaves like a pure microgel particle. Moreover, using this model the particle radius at the interface as well as the stretching factor β are accessible via the core size and shell thickness of the CSNP.

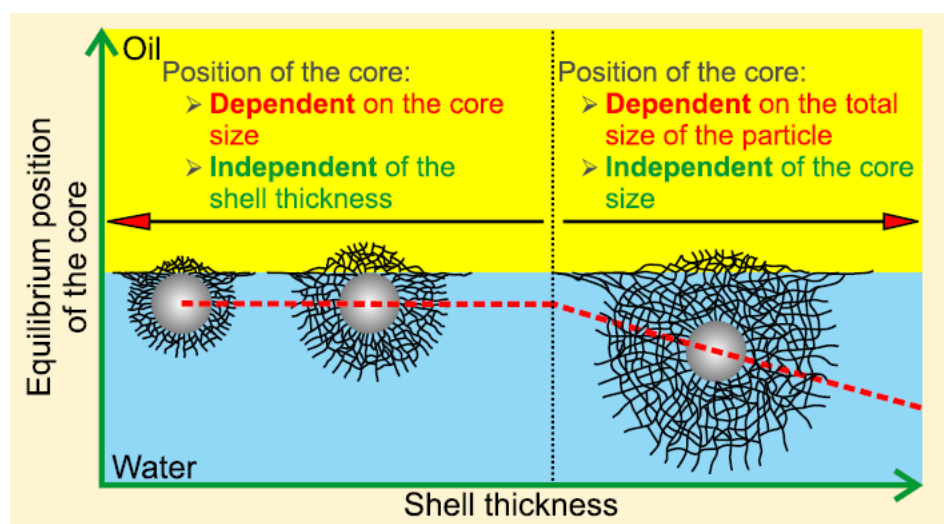


Figure 1.30 Schematic description of the equilibrium position of CSNP in dependence of the shell thickness. Reprinted with permission from Ref. ²⁸⁸. ©2018 American Chemical Society.

Qualitatively, these results can be transferred to air/water interfaces because a similar behavior can be witnessed experimentally at oil/water and air/water interfaces. The main driving force for the particle to adsorb to the interface is the reduction of the interfacial tension. Since the interfacial tension between air and water (72 mN/m) is larger than between decane/hexane and water (50 mN/m) the particles should adsorb even better to the interface since the free energy term becomes larger. The wettability of the particle should be similar in the air/water and oil/water system. Consequently, also for CSNPs at air/water interfaces one can expect a regime, where the equilibrium position of the core depends on the core size and one where it depends on the shell size as depicted in Figure 1.30 for the hexane/water case. Furthermore, this equilibrium position is then again determining the particle radius R_i and stretching factor β .

In contrast to hard colloids where charges can lead to a strong Coulomb repulsion²⁸², which even dominate over capillary attraction²⁹⁶, it was found that charged microgels do not directly show an increased charge repulsion. The charges do not necessarily lead to a decreased compressibility but affect the entire swelling behavior. Analysis of compression isotherms of charged and uncharged P(NIPAM-*co*-methacrylic acid (MAA)) microgel particles showed that the general processes during compression are the same for both particle types but the charged particle properties lead to a higher compressibility of the charged particles before an increase in surface pressure is observed.²⁹⁷

The knowledge of the behavior of colloidal particles in dispersion and at the interface can be used to prepare controlled particle assemblies. The next chapter gives a general overview of 2D assembly methods and particularly of interface-mediated methods.

1.3.3 Assembly Methods

Colloidal self-assembly can produce either 3D colloidal crystals or 2D colloidal monolayers depending on the preparation method and conditions. For 3D colloidal crystals, sedimentation, centrifugation, spray deposition and shear alignment are typical methods, which have been studied extensively. Methods that can render 3D or 2D assemblies depending on the preparation conditions are for example electrodeposition, assembly at liquid interfaces, doctor blading, vertical lifting techniques, drop casting, and spin-coating.

Most of these methods are based on convective assembly, where immersion capillary forces and solvent evaporation play a major role. At the 3-phase-contact line of an aqueous particle dispersion with a hydrophilic solid substrate and the surrounding air, a thin liquid film is formed. This film leads to two important effects: Attractive immersion capillary forces evolve, as soon as the liquid film is thinner than the particle diameter (compare chapter 1.3.3.1). These

forces drag the particles together and into the colloidal crystal. Additionally, the evaporation of this thin solvent film causes a convective flow in the region behind that and transports the particles from the bulk dispersion to the three-phase-contact-line.^{279, 298-300} This enables continuous film formation and, depending on the particle concentration, humidity and evaporation rate, 2D or 3D assemblies can be obtained. For reproducible and high quality assemblies, a tight control and optimization of the process parameters is indispensable for all methods.

1.3.3.1 Direct Assembly Methods

For example, drop casting of a colloid dispersion onto hydrophilic substrates is a very easy approach for the preparation of colloidal crystals by convective assembly and controlled evaporation. However, the preparation of controlled large area and defect free assemblies is difficult to achieve due to meniscus pinning and coffee stain effects.^{298, 301} One method to overcome this obstacle is to slowly move the meniscus in a controlled manner across the substrate. This can either be achieved by vertical deposition³⁰² (dip-coating, Figure 1.31 (a)-(c)) or by horizontal deposition³⁰³ (doctor blading). For vertical deposition, a substrate is partially immersed into the particle dispersion and then slowly retracted at a constant speed. Like this, an ordered colloidal crystal is formed at the drying front of the substrate due to above introduced immersion capillary forces and the particle replenishment due to the convective flow. By tight control over the process parameters, monolayers^{302, 304} or well-ordered multilayer structures³⁰⁵ can be formed. However, process optimization is very tedious due to the many process parameters like dispersion concentration, withdrawal speed, wettability of the substrate, humidity or temperature. Already small changes lead to a failure of the process. Especially the continuous change in concentration due to particle deposition and solvent evaporation during the deposition process impedes the homogeneous coverage of large substrate areas.³⁰⁶ For horizontal assembly, the same forces, rules and process difficulties apply. Here, a substrate is moved horizontally while a fixed confinement creates the receding contact line as depicted in Figure 1.31 (d)-(f).^{303, 307}

In order to realize the preparation of monolayers within minutes and on large areas spin-coating can be employed (Figure 1.31 (g)-(i)). While still relying on immersion capillary forces for the ordered assembly, it is difficult to achieve a long-range order due to high lateral shear forces and fast solvent evaporation with standard protocols.³⁰⁸⁻³⁰⁹ Thus, the assembly is “frozen”, before the particles can reach their minimum energy position within the lattice. However, sophisticated protocols with optimized volatility of the dispensing medium³¹⁰, rotational speeds

and acceleration profiles³¹¹⁻³¹² can yield large area monolayers with a high degree of order, three-dimensional crystals³¹³ or non-close packed monolayers.³¹⁴⁻³¹⁵

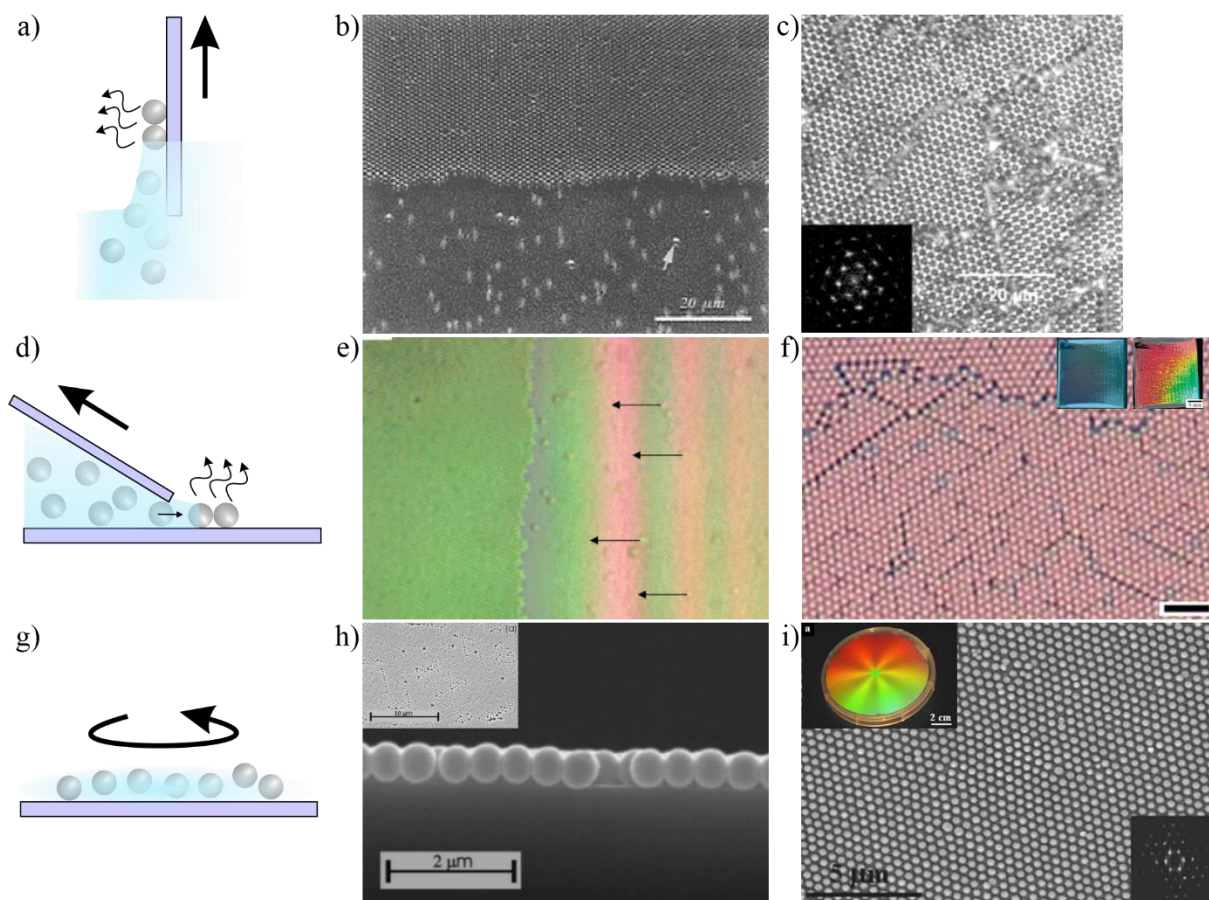


Figure 1.31 Examples for direct assembly methods: (a) Schematic depiction of the dip-coating process leading to 2D particle assemblies. Examples of this method showing experimental PS particle monolayers (b) during the assembly recorded with a horizontally placed video-microscope and (c) on a glass substrate with the corresponding Fast Fourier Transformation (FFT) revealing the six-fold symmetry characteristic for hexagonally ordered arrays. (d) Schematic description of doctor blading and two examples: (e) Monolayer of 500 nm PS particles during assembly recorded with an optical microscope. The receding contact line is clearly visible (f) Optical microscope image of a hexagonally ordered array prepared by doctor blading. Insets show photographs of the cm-sized substrate illuminated from the top and at an angle revealing the iridescent color originating from structural ordering. (g) Schematic depiction of the spin-coating process with two examples of resulting monolayers in (h) close-packed nanoparticle arrays and (i) wafer-scale (see inset) non-close packed nanoparticle array. (b) Reprinted with permission from Ref. ³⁰². ©1996 American Chemical Society (c) Reprinted with permission from Ref. ³⁰⁴. ©2002 American Chemical Society. (e) Reprinted with permission from Ref. ³⁰³. ©2007 American Chemical Society. (f) Reprinted with permission from Ref. ³⁰⁷. ©2004 American Chemical Society. (h) Reprinted with permission from Ref. ³¹⁰. ©2006 WILEY-VCH. (i) Reprinted with permission from Ref. ³¹⁴. ©2006 American Institute of Physics.

1.3.3.2 Directed Assembly Methods

With template assisted self-assembly in combination with the above introduced methods, more complicated, hierarchical structures and control over the particle orientation can be achieved. The substrates can be either patterned topographically³¹⁶⁻³¹⁸ or chemically with spatially altered wettability³¹⁹⁻³²², functional groups³²³⁻³²⁴ or surface charges.^{271, 325-327} Topological templates that offer high precision structures and basically unlimited access to complex structures are usually prepared by e-beam lithography.³²⁸⁻³³⁰ These structures can then be used as substrate during capillarity-assisted particle assembly (CAPA), where horizontal assembly is used to deposit the particles into the template voids by controlled evaporation at the three-phase-contact line as depicted in Figure 1.32 (a)/(b).^{316, 331-332}

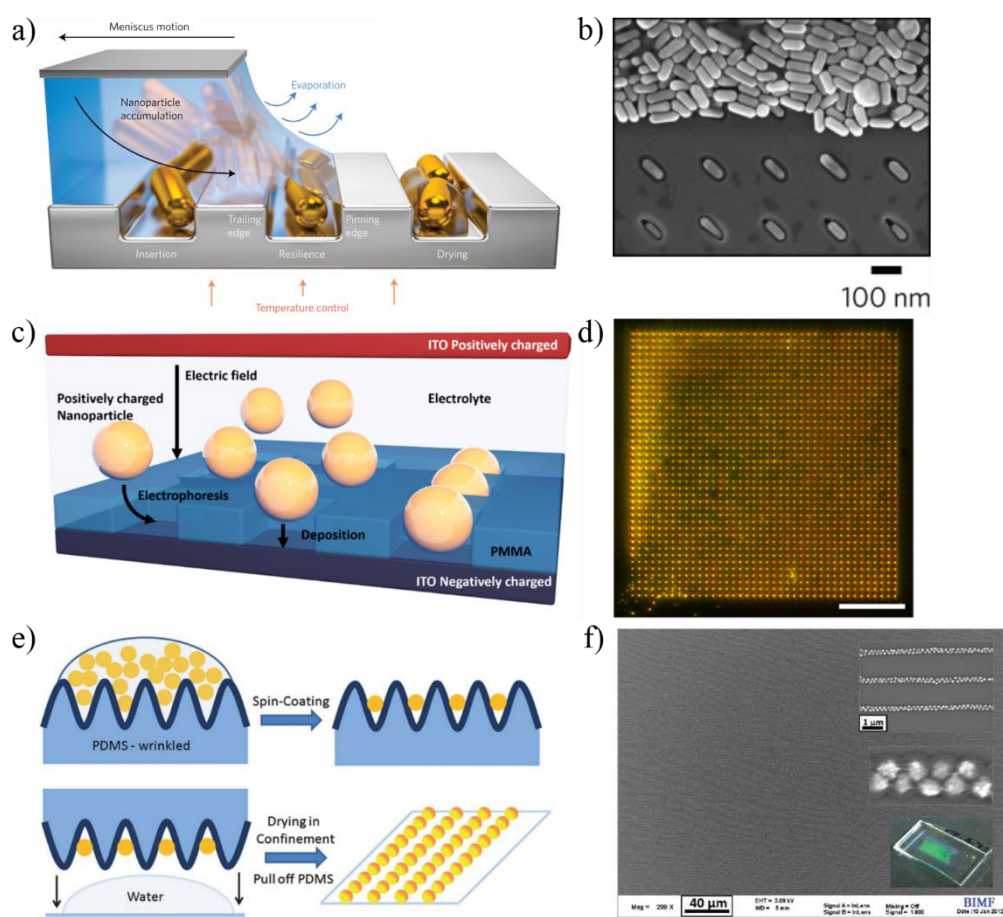


Figure 1.32 Examples for directed assembly methods: (a) Schematic illustration of the capillarity-assisted particles assembly (CAPA) process and (b) SEM image of resulting structure presented by Flauraud in 2017. (c) Schematic description of template-assisted electrophoretic assembly and (d) resulting monolayer published by Zhang *et al.* (e) Schematic description of winkle-assisted nanoparticle deposition leading to ordered nanoparticle lines as depicted in (f). (a, b) Reprinted with permission from Ref. ³¹⁶. ©2016 Springer Nature. (c, d) Reprinted with permission from Ref. ³³³. ©2018 American Chemical Society. (e) Reprinted with permission from Ref. ²⁵⁰. ©2012 The Royal Society of Chemistry. (f) Reprinted with permission from Ref. ¹¹⁴. ©2012 American Chemical Society.

The receding meniscus pins to the protruding features leading to a directed deposition into recesses of the features.^{303, 334-336} Zhang *et al.* (Figure 1.32 (c)/(d)) combined the template assisted approach with electrophoretic deposition allowing precise and controlled directed assembly of positively charged, spherical and rod-shaped gold nanoparticles onto a negatively charged patterned substrate.³³³ Here, large area assemblies were obtained but the template preparation is very time and money consuming. A very cheap and large area approach, which is, however limited to line structures, is the employment of centimeter-scaled wrinkled structures (Figure 1.32 (e)/(f)).^{318, 337-338} For the wrinkle formation, a flat slab of the elastomer polydimethylsiloxane (PDMS) is stretched and the elastic modulus of the surface layer is increased by plasma hardening. Upon release, a wrinkled surface structure is formed. Into those wrinkles particles can be deposited by drop-casting, spray-casting³³⁹, spin-coating^{337 114, 250} or dip-coating.^{318, 340} Finally, the assembled structures can either be used directly in the template or be transferred to the desired substrate.^{114, 250, 340}

1.3.3.3 Interface-Mediated Methods

High degrees of order can also be achieved by interface mediated assembly methods. These methods inherently yield hexagonally ordered 2D particle monolayers at a liquid/liquid or gas/liquid interface, which can then be transferred to a solid substrate in a second step. Classically, Langmuir troughs (Figure 1.33 (a)/(d)) are used for particle assembly of hard spheres like silica, PS or PMMA colloids at the air/water interface as they yield high quality assemblies.³⁴¹⁻³⁴⁴ First, particles are applied to the air/water interface by spreading the particles from a suitable dispersion medium. The particles form a loose monolayer at the interface where the particle can move laterally independent from each other. Then, the barriers are moved together, reducing the free interfacial area. At the beginning, this is accompanied by no change in lateral pressure because the particles are not yet in contact and still move freely at the interface. Upon further reduction of the interfacial area, the particles come into contact and close-packed domains are formed due to capillary attraction accompanied by an increase in lateral pressure. Finally, a close packed particle monolayer with different domains will be formed at the highest lateral pressure. When the monolayer is further compressed, buckling of the monolayer takes place, resulting in a destroyed monolayer and an abrupt decrease in surface pressure. The quality of the formed monolayer depends on the interaction forces between the particles and can thereby for example be tuned by particle charge and pH value of the subphase.³⁴³ An obvious advantage of the Langmuir technique is the high reproducibility of the process mainly due to the possible monitoring of the monolayer formation via optical microscopy or surface pressure-area isotherms.

In a similar but more simple approach, the assembly is conducted in an ordinary crystallizing dish and the particles are applied to the air/water interface through a thin cannula (Figure 1.33 (b)/(e)).³⁴⁵ The tip is brought into contact with the interface until a meniscus is formed. Upon application of the dispersion the particles are radially pushed away from the tip and a close-packed particle monolayer starts to grow from the rim of the crystallizing dish. This behavior is driven by the Marangoni effect and by careful control of the particle concentration, water/alcohol ratio of the dispersion medium and the subphase properties, large area monolayers of fairly high quality can be generated.

Instead of applying the particles directly to the interface, a hydrophilic glass substrate is used as intermediate step by Vogel et al (Figure 1.33 (c)/(f)).³⁴⁶ The substrate is immersed into the aqueous phase at a 45° angle and the particles, dispersed in a water/ethanol mixture, are applied to the substrate. When the flow front hits the three-phase contact line (substrate/water/air) a close-packed particle monolayer will be directly formed. This method effectively pins the particles to the interface, avoiding defects from particle flow into the bulk subphase.

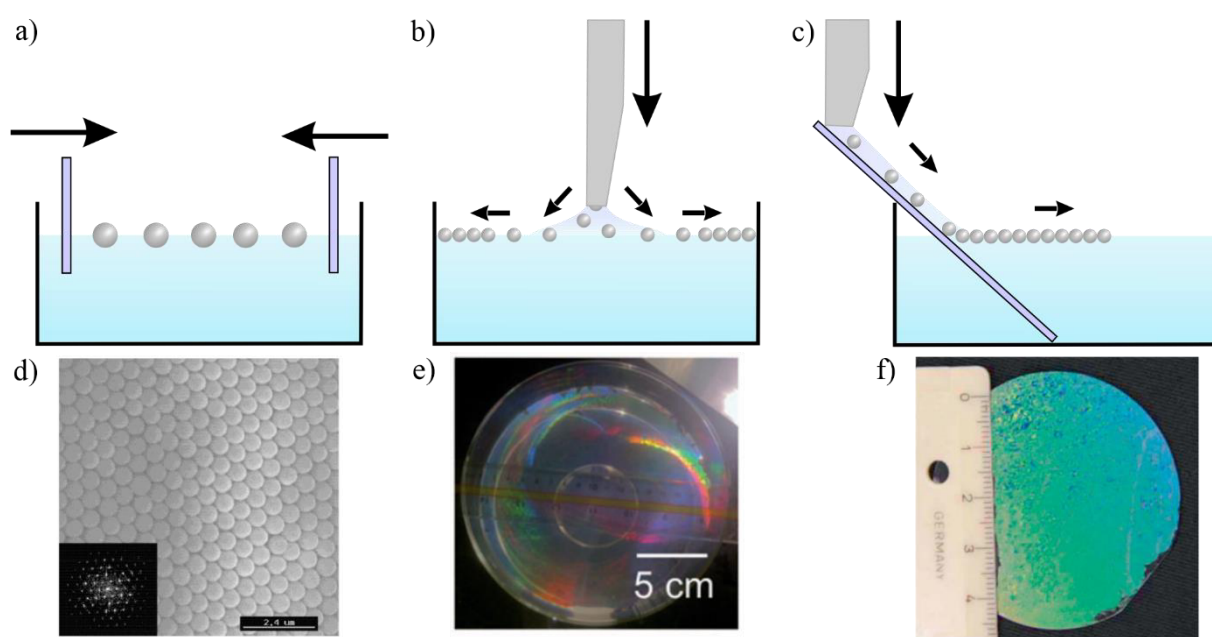


Figure 1.33 Interface-assisted self-assembly. (a) Langmuir trough technique (b) direct application to interface (c) Application over a glass substrate (d) Close-packed monolayer obtained by Langmuir trough technique. (e) Photograph of crystallizing dish with iridescent particle monolayer at the air/water interface. (f) Photograph of Si-wafer carrying a homogeneous particle monolayer from interface assembly via a glass slide. (d) Reprinted with permission from Ref. ³⁴². ©2003 American Chemical Society. (e) Reprinted with permission from Ref. ³⁴⁵. ©2012 WILEY-VCH. (f) Reprinted with permission from Ref. ³⁴⁶. ©2011 WILEY-VCH.

A combination of spin-coating and interface-assisted assembly was introduced by Retsch *et al.*³⁰⁶ First, negatively charged PS particles are spin-coated on a cationically functionalized

glass substrate. Then, this substrate is immersed into an aqueous subphase. The particles detach at the three-phase contact line (glass substrate/water/air) and form a close-packed particle monolayer due to attractive capillary floatation and immersion forces.

The monolayers formed by the interface-mediated methods introduced above can be collected onto solid substrates using different methods. Either vertical (Langmuir-Blodgett) transfer^{290, 347-348}, removal of the subphase^{289, 343, 349-350} or manual immersion of a substrate and withdrawal under a shallow angle where the monolayer attaches during retraction^{253, 306, 346} can be employed.

1.3.4 Formation of Non-Close Packed Nanoparticle Assemblies

The so far introduced interface-mediated methods usually yield close-packed, hexagonally ordered particle arrays when hard, incompressible particles are used. Non-close packed arrays can for example be obtained by monolayer formation at oil/water interfaces instead of air/water interfaces.^{275, 281, 351-352} This indicates that the balance of forces is shifted from dominating attractive forces at air/water interfaces to repulsive electrostatic forces at oil/water interfaces. The center-to-center distances can now be tuned by the amount of particles added to the interface. One difficulty is to maintain the non-close packed pattern formed when the particles are transferred to solid substrates. Here, strong capillary and viscosity forces can drive the particle together during drying. Selecting hexane as oil phase enables transfer of the interfacial structure, as it possesses a low viscosity and high volatility.^{275, 281} Post modification of the particle monolayers is another possibility to realize non-close packed structures. Polymeric nanoparticles can be plasma-etched in order to reduce their size and create non-close packed arrays (compare Figure 1.34 (a) prior and (b) after etching) while maintaining the original center-to-center distance.^{346, 353-354} Alternatively, the transfer of the monolayers to elastomeric substrates enables the formation of non-close packed arrays by substrate swelling, circular stretching or stretching in the x and y direction simultaneously.³⁵⁵ For circular stretching, the close packed array is first transferred to a PDMS substrate, stretched in the chosen direction and then transferred to a new PDMS substrate. Next, the stretching process is repeated with a different angle with respect to the lattice. This process opens the pathway to other structures like non-close packed lines, oblique angle, rectangular and square non-close packed particle assemblies.³⁵⁵ A very elegant approach to achieve these patterns was presented recently by Hummel and Stelling.³⁵⁶ First, they prepared hexagonally close-packed PnBA-co-PMMA particle monolayers at an air/water. Then, the particles were transferred onto hydrophobic substrates by submerging the substrate through the monolayer into the subphase. Thereby, the

monolayer was stretched into a non-close packed array. Depending on the stretching factor, which can be controlled by the substrate contact angle with the subphase, and the stretching angle, all 2D Bravais lattices were achieved. As a last step, the particles were immobilized via thermal annealing near the glass transition temperature of the particle or the substrate in order to stabilize the array against drying effects. Figure 1.34 (c)-(g) depict the resultant lattices.

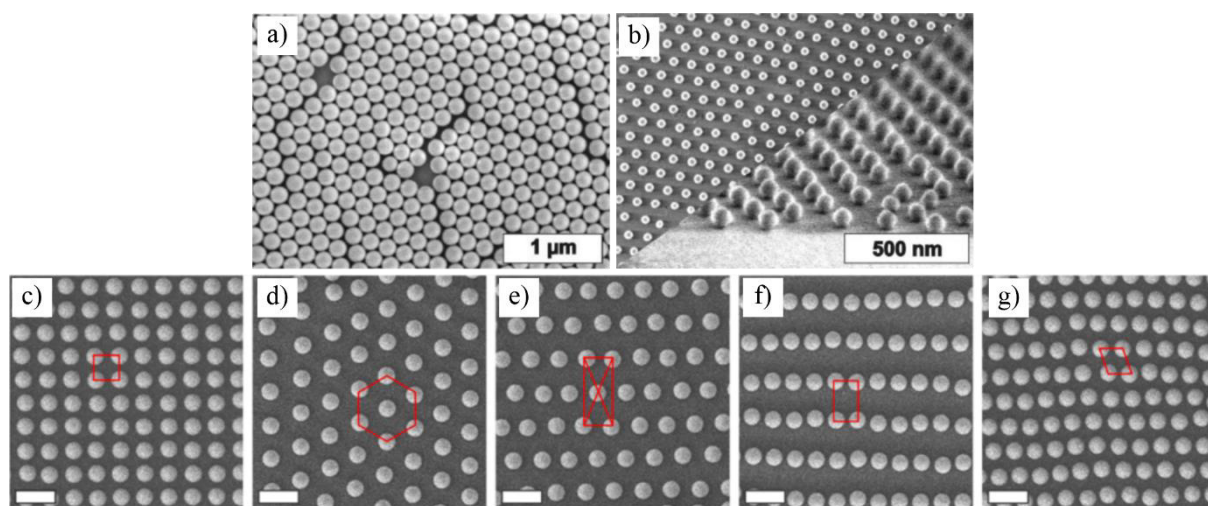


Figure 1.34 Examples for the formation of non-close packed arrays. (a) SEM image of a close-packed monolayer of surface-attached colloids ($d = 180\text{nm}$) as deposited and (b) after 1.5 min of etching (Ar, 5 sccm, 190 W). (c) to (g) Particle array symmetries obtained by the deformation of the monolayer upon the transfer to a hydrophobic substrate. Particle monolayers are stretched to yield the five possible Bravais lattices in the two-dimensional space (c) to (g): Square, hexagonal, centered rectangular, rectangular, and oblique. (Scale bars: $1\text{ }\mu\text{m}$). (a,b) Reprinted with permission from Ref. ³⁵³. ©2009 Wiley-VCH. (c-g) Reprinted with permission from Ref. ³⁵⁶. ©2018 American Chemical Society.

Another method to form non-close packed particle monolayers employs hard cores with a soft deformable shell. Depending on the chosen shell size, the interparticle distance can be tuned between the sub-nm range and several hundreds of nanometers.²⁵⁸ For example, Au nanoparticles, stabilized by citrate, have sub-nm interparticle distances in the dried state. This distance increases to about 1 nm when trialkyl ammonium bromide ligands are used. Linear polymer ligands of PS³⁵⁷ or PNIPAM²⁵⁶ can for example be used for interparticle distances between 5 and 41 nm, depending on the chosen molecular weight. Even larger interparticle distances up to several hundreds of nm can be obtained by nanoparticle encapsulation into dense polymer shells³⁵⁸ or deformable microgel shells.^{249, 251, 253, 359} As soft particles and/or shells can be compressed, the center-to-center distances can be dynamically tuned depending on the available surface area per particle at the interface.^{290, 349, 360-361}

The influence of a hard, inorganic core on the interparticle interaction at the interface and thus on the assembly behavior can be shown when comparing the works of Rey *et al.*³⁶⁰ and Rauh

*et al.*²⁹⁰ Rey *et al.* used pure microgel particles, which consist of a highly cross-linked volume element as "core" and an outer, more loosely cross-linked part as "shell". This is not to be confused with the incompressible inorganic hard cores used in the work by Rauh *et al.* in Figure 1.35 (a) and (b) the compression curves of pure microgel particles and hard-core/soft- microgel shell particle monolayers are shown, respectively. For both systems, the Langmuir trough method at a hexane-water interface is employed. The curves appear to have an analogous trend. In the first phase, at large specific areas, very low surface pressures (I/i) are observed. This is followed by a second phase with a steep increase in surface pressure (II/ii) and a third plateau phase (III/iii). Just before monolayer buckling in phase five (V/v), a small surface pressure region (IV/iv) can be found where the last stable assembly is formed. Analyzing the microstructures of monolayers extracted during the different phases of assembly (green boxes: microgel particles; red boxes: hard-core/soft-shell particles) major differences become visible. For hard-core/soft-shell particles with limited shell thickness, loosely packed hexagonally monolayers are initially formed. Large holes are visible in the assembly when a large area per particle is available. This inhomogeneous particle distribution is caused by the increased attractive capillary forces between the particles due to the hard core as compared to pure microgel particles.²⁹⁰ Under the same conditions, pure microgel particles form a homogeneous gas like phase (i/I). Next, just when the surface pressure starts to increase significantly, hexagonally ordered monolayers are formed with both particle types. Here, all particles are in shell-to-shell contact (first hexagonal phase; II-b, ii). Upon compression, the behavior of hard-core/soft-shell particles again deviates from pure microgel particles. For the microgel particles a constant deformation (compression) of the whole lattice (decrease of area per particle in phase II-e)²⁹⁷ can be witnessed over a certain range of area/particle resulting in a significant decrease in the center-to-center distance d_{c-c} . The hard-core/soft-shell particles quickly form clusters within the hexagonal array, where particles are in core-to-core contact (second hexagonal phase, phase iii). At the same time, the d_{c-c} of the particles still in shell-to-shell contact hardly decreases. Upon further compression, the number of aggregated clusters in core-to-core contact increases.²⁹⁰ The phase transition from shell-to-shell into core-to-core contact also occurs for the pure microgel particles with an increasing core-to-core fraction as the available area per particle is progressively reduced (phase III-b and III-e). The last compression step again depends on the type of particles used. In hard-core/soft-shell systems, monolayer buckling will occur before all particles are in core-to-core contact (phase v).²⁹⁰ On the other hand, a closest packed, hexagonally ordered monolayer in core-to-core contact is formed with pure microgel particles (phase IV)^{297, 360-361} prior to monolayer buckling (phase V). When core/shell particles

with large shells are used their behavior converges towards the behavior of pure microgel particles. This leads to slightly tunable interparticle distances in the shell-to-shell contact regime in the work of Rauh *et al.*²⁹⁰ in the case with the largest shell to core ratio of 3.3 prior to cluster formation. In contrast to hard colloids, where the aggregation at an interface is usually irreversible, the compression of microgel particles is reversible.²⁹⁷

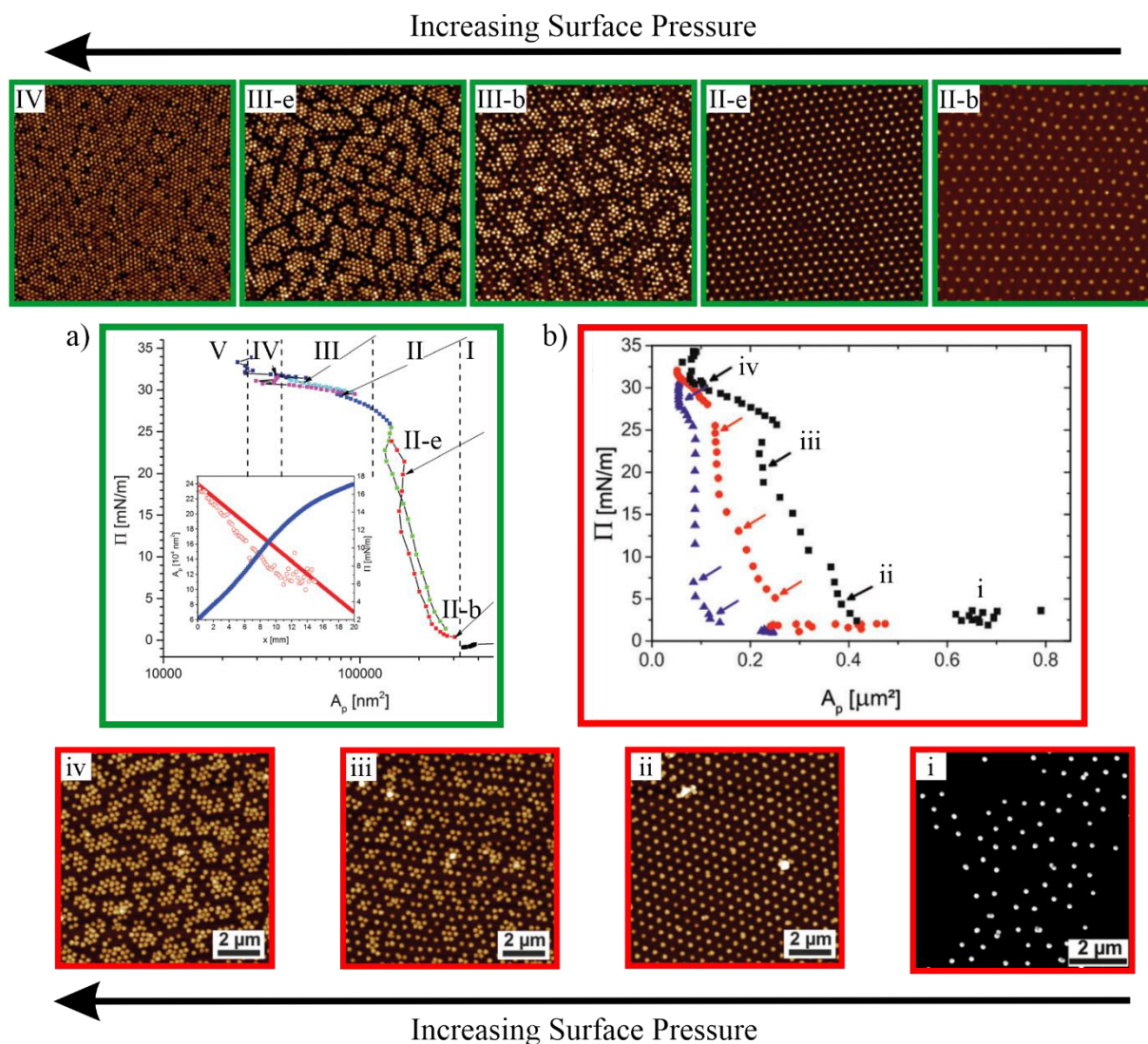


Figure 1.35 Pure soft microgel (green) and hard-core/soft-microgel shell particles (red) at an oil/water interface. (a) and (b) Compression isotherms with the surface pressure Π in dependence of the area per particle A_p . Important phases are labelled I to V of the pure microgel (a, green boxes) and i to iv for the hard-core/soft-shell (b, red boxes) particles. The top and bottom rows show SEM/AFM images of the collected particle monolayers collected at different positions in the compression isotherms. Adapted with permission from Ref.³⁶⁰. © 2016 The Royal Society of Chemistry. and from Ref.²⁹⁰ © 2016 The Royal Society of Chemistry.

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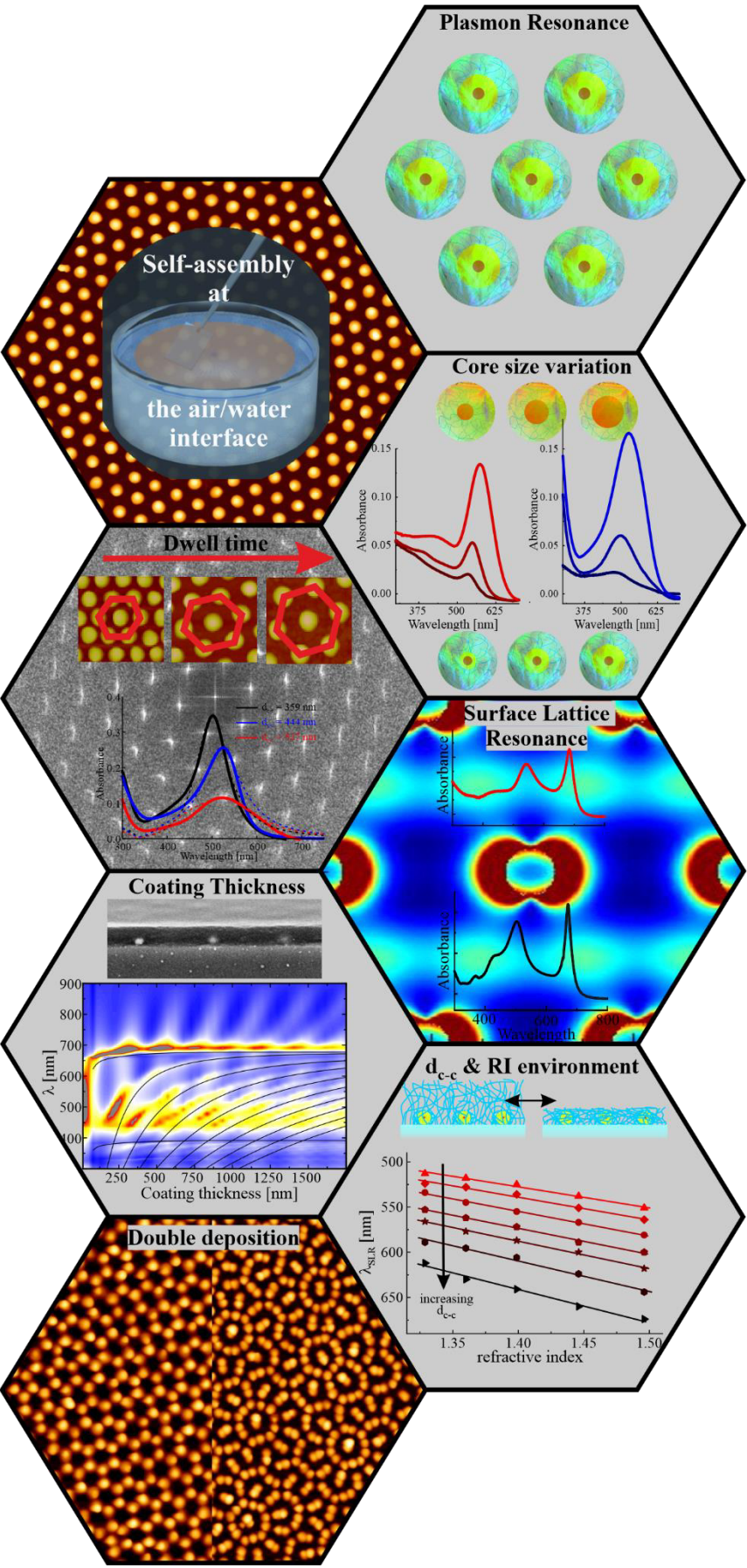
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2 Overview of the Thesis



2.1 Summary of Individual Contributions

2.1.1 Tunable Plasmonic Surfaces via Colloid Assembly

The first publication in the course of this thesis presents the fabrication of plasmonic particle surfaces. Spherical gold (Au) and silver (Ag) nanoparticles of different sizes, encapsulated in a cross-linked poly-*N*-isopropyl acrylamide (PNIPAM) shell, were assembled into uniform, hexagonally ordered arrays via self-assembly. The macroscopic particle monolayers were analyzed with atomic force microscopy (AFM) and far-field absorbance UV-vis spectroscopy. The optical response of the different arrays, which possess the same numbers of particles per area, solely depends on the plasmonic core size and type of employed particle batch.

For this, spherical gold nanoparticles of 20 nm in diameter were encapsulated into a PNIPAM shell using a seeded precipitation polymerization protocol with *N,N'*-methylenebisacrylamide (BIS) as a cross-linker. Next, the gold cores of the core/shell particles were overgrown either with gold or with silver using adapted seeded-growth protocols. Like this, ten particle batches with identical polymer shells but varying core sizes and materials were obtained. The core sizes of the spherical particles are in the range between 20 nm and 100 nm in diameter as depicted in Figure 2.1 (b) with representative absorbance spectra in solution for Ag@Au-PNIPAM in (a) and Au@Au-PNIPAM in (c).

For the self-assembly of the particles at the air/water interface, a protocol from Vogel *et al.*² was adapted for hard-core/soft-shell particles. Therefore, a concentrated particle dispersion (1-2 wt.-%) in a water/ethanol mixture (50:50 vol.-%) dispensed onto a tilted glass slide, which was half-way immersed into an aqueous subphase. When hitting the air/water-interface, a hexagonally ordered monolayer formed spontaneously. Like this, floating monolayers with variable particle core sizes were obtained. These monolayers were transferred to glass slides without losing the order of the assembled particle lattices.

We found that the core-to-core distance (d_{c-c}) at the interface is mainly defined by the PNIPAM shell diameter. In dispersion, dynamic light scattering determined a hydrodynamic radius of approximately 323 nm for all particle batches. Therefore, nearly identical d_{c-c} 's of approximately 460 nm were obtained for all employed particle systems (particle densities of 4.65 particles per μm^2). The difference of the hydrodynamic core/shell diameter in dispersion and the d_{c-c} of the particle monolayer of more than 100 nm, points to an anisotropic deformation of the hydrogel shell at the interface. The uniform surface coverage allowed for the formation of plasmonic surfaces, where the plasmonic response can be tuned solely by the employed core particle system.

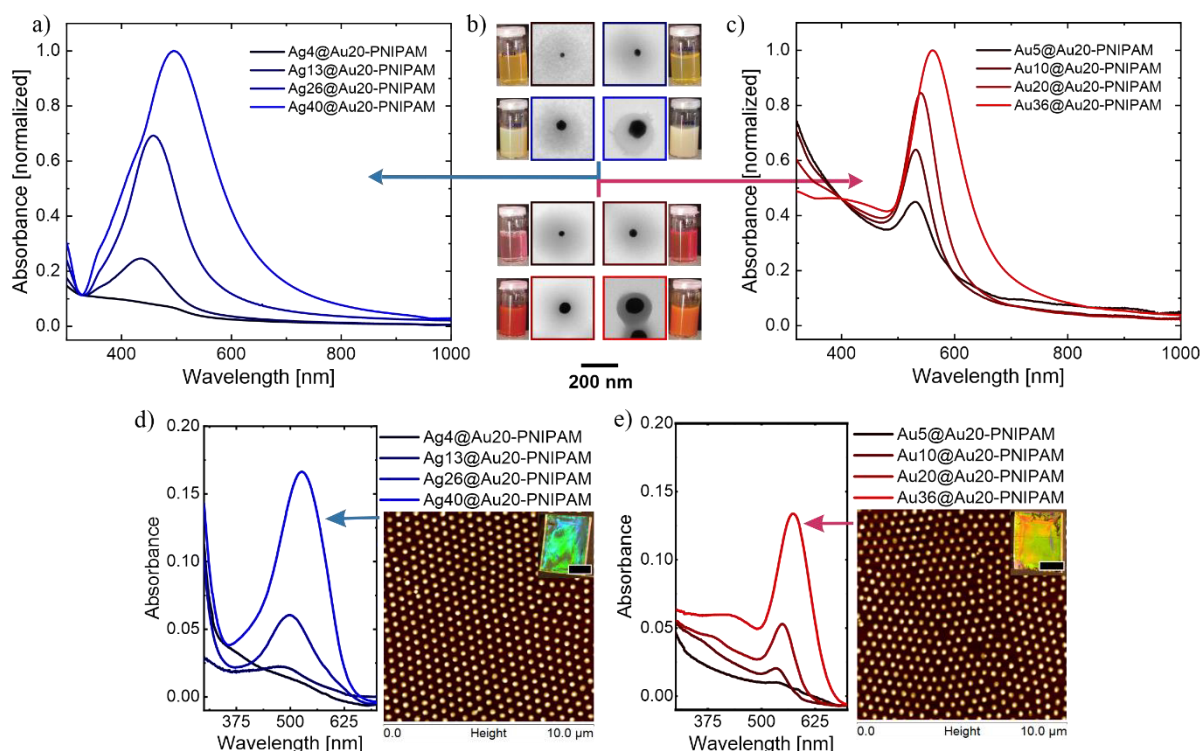


Figure 2.1 Tunable plasmonic surfaces via self-assembly of plasmonic nanoparticles. UV-vis absorbance spectra of (a) Ag@Au-PNIPAM particles and (c) Au@Au-PNIPAM with increasing thickness of the silver/gold shell. (b) Shows TEM images of the different core/shell particles accompanied by photographs of the particles in aqueous dispersion (Top: Ag@Au-PNIPAM particles; Bottom: Au@Au-PNIPAM particles). UV-vis absorbance spectra of the hexagonally ordered monolayers (d) of Ag@Au-PNIPAM particles with increasing silver shell thickness (black to blue trace) and (e) Au@Au-PNIPAM with increasing gold shell thickness (black to red trace). All monolayer possess similar center-to-center distance d_{c-c} of approximately 460 nm. Two exemplary AFM images of the monolayers with the largest metal cores are depicted in (d) with Ag40@Au20-PNIPAM and (e) Au36@Au20-PNIPAM accompanied with a photograph of the respective monolayer on glass as inset. Adapted with permission from Ref. ¹. ©The Royal Society of Chemistry 2015.

For all particle systems, the optical properties of the plasmonic surfaces followed the same trend as in dispersion (Figure 2.1 (d) and (e)). Particles that only have a very thin silver shell (4 nm) around the inner gold core (20 nm) showed a plasmonic response that is not yet characteristic for silver, but a broadened LSPR signal of a mixed silver and gold nature. For the other silver and all gold particles systems, however, a continuous increase of the LSPR wavelength and an increasing absorbance was found as the plasmonic core diameter increases. The LSPR maxima of the silver systems were in all cases at lower wavelengths than the gold particles of the respective size. For silver, the LSPR wavelength increased from 433 nm to 496 nm in dispersion and from 484 nm to 527 nm in the monolayers as the core size increased from 46 nm to 100 nm. The gold particle systems exhibited a red-shifted LSPR response with LSPR wavelengths between 530 nm and 568 nm in dispersion and between 536 and 573 nm as a hexagonally

ordered monolayer on a glass substrate. Consequently, we were able to tune the LSPR wavelength of the plasmonic monolayer between 484 nm and 573 nm depending on the selected colloidal building block. The absorbance intensity of the LSPR maximum was found to be between 0.025 and 0.16 depending on the employed core size at the selected d_{c-c} of 460 nm. Using these findings, macroscopic plasmonic surfaces with a controlled surface coverage and tailored absorbance properties can be created by using a simple wet-chemical synthesis and self-assembly approach.

2.1.2 Time-Controlled Colloidal Superstructures: Long-Range Plasmon Resonance Coupling in Particle Monolayers

The second publication focuses on another possibility to tune the optical response of a particle monolayer. Here, instead of tuning the particle dimensions of the plasmonic particles, the core-to-core distance d_{c-c} was adjusted in a controlled manner. A silver-core/PNIPAM-shell (Ag-PNIPAM) building block with $d_{core} = 100$ nm and $d_{h(20^{\circ}C)} = 336$ nm was chosen. Again, freely floating particle monolayers of about 5 cm in radius were formed at the air/water interface by applying the method from Vogel *et al.*² (Figure 2.2 (a)). Next, the monolayers were transferred step-by-step onto hydrophilic glass substrates of 1 cm^2 as already described in the previous chapter. Between two transfer steps, the monolayers were left to equilibrate for a certain period of time.

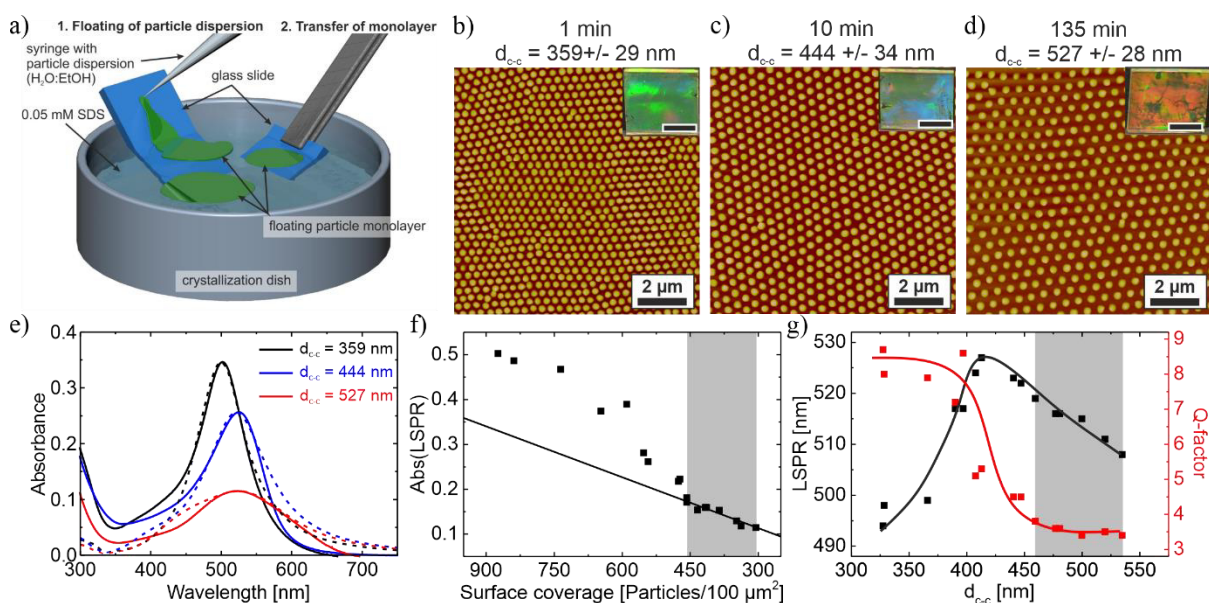


Figure 2.2 Time-Controlled Colloidal Superstructures: Long-Range Plasmon Resonance Coupling in Particle Monolayers. (a) Schematic illustration of the assembly process at the air/water-interface using particle application via a glass slide. (b) to (d) AFM images of hexagonally ordered particle monolayers with increasing d_{c-c} as the dwell time of the particles increases from 1 min (b) over 10 min (c) to 135 min (d). Insets show photographs of the monolayers on glass. The different iridescent colors evolve due to an increasing interparticle spacing. (e) UV-vis absorbance spectra of the monolayers shown in (b) to (d). Solid lines are experimental results and the dotted lines depict results from simulations. (f) Dependence of the absorbance intensity at the LSPR on the surface coverage. The black line indicates the theoretical, linear correlation between absorbance and surface coverage when no coupling between particles takes place. (g) Dependence of the LSPR wavelength (black squares) and Q-factor (red squares) on d_{c-c} . The lines are guides to the eye. Grey shaded areas in (f) and (g) indicate the same samples. Adapted with permission from Ref. ³. ©2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Characterizing the obtained samples using AFM revealed a steady increase in the center-to-center distance (d_{c-c}) of the hard-core/soft-shell particles (Figure 2.2 (b) – (d)). The starting

center-to-center distance of $d_{c-c(1min)} = 359 \text{ nm} \pm 29 \text{ nm}$ was close to the hydrodynamic diameter of the core/shell particles in dispersion, i.e. the particles have not yet stretched out at the interface. With time, however, the particles in the entire monolayer slowly stretched out at the interface minimizing the surface energy. Thus, by giving the system time to equilibrate, increasing center-to-center distances were obtained with every extracted monolayer. The speed of this process is increased by the extraction of parts of the monolayer, when samples are transferred to glass substrates due to the energy, which is brought into the system by movement. Over the course of a dwell time of 135 minutes and the extraction of several samples the d_{c-c} increased gradually to $527 \text{ nm} \pm 28 \text{ nm}$. The hexagonal order of the extracted samples was evaluated using Fast Fourier Transformations (FFTs) and radial distribution functions (pair correlation function $g(r)$). The FFTs revealed strong and distinct Bragg peaks, characteristic for a 2D hexagonally ordered crystal and $g(r)$ showed matching peak positions to a perfectly hexagonally close-packed reference monolayer up to several orders.

Optical characterization of the silver monolayers using absorbance UV-Vis spectroscopy at several sample positions proofed the homogeneity of the assembly over the whole substrate and revealed an absorbance behavior that is strongly distance dependent of the samples (Figure 2.2 (e)). At the smallest $d_{c-c} = 359 \text{ nm}$ ($8.4 \text{ particles}/\mu\text{m}^2$) a narrow LSPR at 500 nm and a maximum absorbance of 0.35 was measured. At an intermediate distance of 444 nm ($5.4 \text{ particles}/\mu\text{m}^2$), a broadened LSPR with a maximum at 522 nm and an absorbance of 0.26 was found. The absorbance decreased further to 0.12 accompanied with the broadest LSPR peak at 524 nm as the d_{c-c} increased to 527 nm ($3.9 \text{ particles}/\mu\text{m}^2$). Concomitantly, the full width at half maximum (FWHM) values of the plasmon resonance peak decrease from 159 nm for the last sample to 62 nm for the sample with the smallest d_{c-c} . This equals Quality factors ($Q_{\text{LSPR}} = \text{LSPR maximum}/\text{FWHM}$) of 3.24 and 8.03 , respectively. The strong increase in Q -factors for small interparticle distances indicates the onset of weak radiative coupling in the particle monolayers.⁴ Additionally, the dipolar coupling is demonstrated by the non-linear behavior of the absorbance intensity when plotted against the particle density (compare Figure 2.2 (f)) as well as the blue-shift of the LSPR wavelength at small d_{c-c} 's (g).⁵⁻⁶ We were able to theoretically describe these findings using a coupled dipole approach. The observed broadening of the resonance at larger interparticle distances is well described by the introduction of an attenuation factor, which limits the range of dipolar coupling by damping the optical response.

2.1.3 Reversible Tuning of Visible Wavelength Surface Lattice Resonances in Self-Assembled Hybrid Monolayers

As the last step towards the formation of surface lattice resonances (SLRs) in self-assembled monolayers the importance of the refractive index environment was closely examined in this publication. So far, I was able to prepare hexagonally ordered monolayer samples that show characteristics of weak dipole/radiative far-field coupling at relatively small interparticle spacings. However, the strong, narrow absorbance peaks that are characteristic for far-field dipolar lattice coupling were not obtained, yet. From lithographically prepared samples we know, that two important prerequisites need to be fulfilled in order to obtain strong far field coupling- I) the lattice constant needs to be in the same wavelength range as the single particle LSPR. II) Coupling between the LSPR and the lattice mode requires a homogeneous refractive index environment.

The first requirement can easily be achieved by using the previously presented self-assembly approach at the air/water interface. Here, I slightly modified the sample preparation technique by directly applying the particle dispersion onto the air/water interface using an Eppendorf pipette comparable to the method employed by Zhang *et al.*⁷ Additionally, no SDS was added to the aqueous phase in the crystallizing dish and the particles were dispersed in pure ethanol. This did not influence the extension behavior of the resulting monolayer, however a larger uninterrupted monolayer was available because no microscope slide had to be inserted into the crystallizing dish.

For the second requirement, I chose three different approaches:

i) To realize a homogeneous refractive index environment, a 244nm thin PNIPAM film with benzophenone, acting as cross-linker, was spin-coated on top of the plasmonic array (Figure 2.3 (a)). After UVA treatment, a cross-linked PNIPAM film possessing a refractive index close to the refractive index of the glass substrate ($RI_{\text{glass}} = 1.52$) was obtained. The particles used in this study were Ag-PNIPAM core/shell particles with $d_{\text{Ag}} = 102 \pm 7$ nm (TEM) and $d_{\text{h}(20^\circ\text{C})} = 326$ nm (DLS). After self-assembly the particles exhibited an interparticle distance of $d_{\text{c-c}} = 450 \pm 31$ nm. As shown in Figure 2.3 (b), a rather broad dipolar LSPR with a maximum at 550 nm was recorded prior to the coating using UV-vis absorbance spectroscopy for the particles assembled on the glass slide (red trace). The red shift of the LSPR compared to the particles in dispersion (LSPR = 505 nm, black trace) can be explained by the effective increase of the RI environment from water ($RI_{\text{water}} = 1.33$) to a mixed environment composed of the glass substrate ($RI_{\text{glass}} = 1.52$), the collapsed PNIPAM shell ($RI_{\text{PNIPAM}} = 1.49$, incl. residual water) and air (RI_{air}

=1.00). Additionally, the narrowing of the resonance from a $\text{FWHM}_{\text{dispersion}} = 200 \text{ nm}$ to $\text{FWHM}_{\text{monolayer}} = 100 \text{ nm}$ points towards a weak dipole/radiative coupling within the monolayer.³ After coating with the PNIPAM film, the coupling strength was increased due to the homogeneous refractive index environment. Consequently, plasmon resonance coupling with the diffractive mode was achieved resulting in a hybrid mode with a resonance peak at 594nm (blue trace). The classification as surface lattice resonance (SLR) was confirmed by FDTD simulation with the reproduction of the experimental spectra shown in (c) and the additional, enhanced field intensity between the particles in the near-field electromagnetic intensity map $|E/E_{\text{inc}}|^2$ compared to the not coated particle monolayer depicted in (d) (visible as green/blue area). After a first device with a narrow SLR ($\text{FWHM}_{\text{device}} = 43 \text{ nm}$, $Q\text{-factor} = 13.8$) was achieved based on self-assembled plasmonic building blocks, the influence of the refractive index environment and dc-c was studied in more detail.

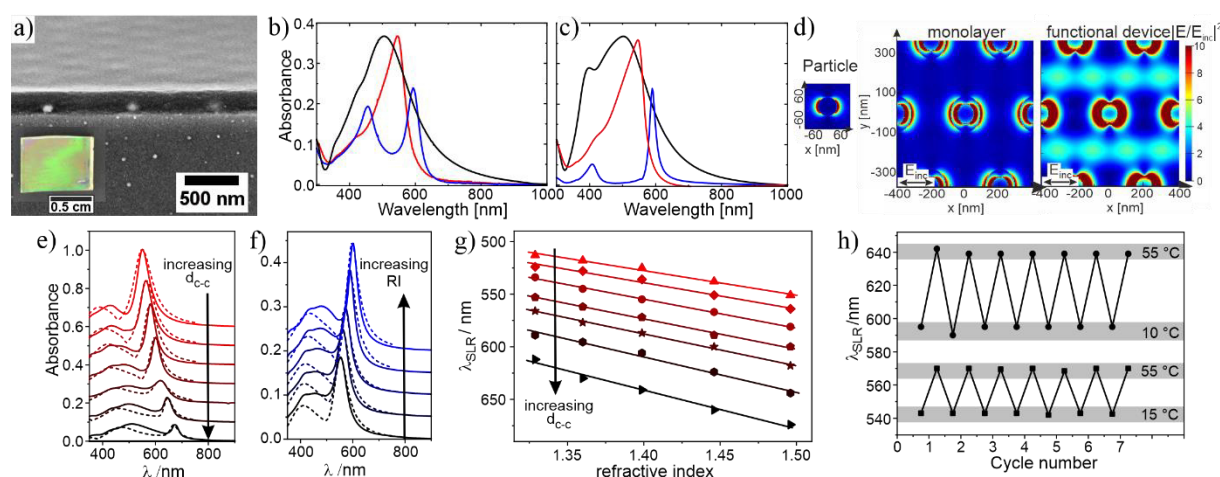


Figure 2.3 Reversible Tuning of Visible Wavelength Surface Lattice Resonances in Self-Assembled Hybrid Monolayers. (a) Side-view SEM image of Ag-PNIPAM monolayer coated with a 240 nm cross-linked PNIPAM film with a photograph of the whole sample as inset. (b) Experimental UV-vis absorbance spectra of Ag-PNIPAM particles in aqueous dispersion ($d_{\text{Ag}} = 102 \pm 7 \text{ nm}$ and $d_{\text{h}(20^\circ\text{C})} = 326 \text{ nm}$, black trace), a hexagonally ordered particle monolayer on glass against air of the same particles ($d_{c-c} = 450 \pm 31 \text{ nm}$, red trace) and the same monolayer after coating with a cross-linked PNIPAM film ($d_{\text{film}} = 240 \text{ nm}$, functional device, blue trace). (c) Respective spectra calculated with FDTD simulations and (d) the supplementary electronic field maps. UV-vis absorbance spectra demonstrating the effect of dc-c (e) and refractive index (f) on the SLR wavelength. The solid lines are experimental results and the dashed lines calculated spectra from coupled dipole approximation (CDA). (g) Summary of the effect of dc-c and refractive index on the SLR wavelength. (h) Reversible SLR wavelength tuning depending on the swelling and collapse of the PNIPAM coating with temperature. Square symbols show the results of a particle monolayer with $d_{c-c} = 430 \text{ nm}$ and circular symbols with $d_{c-c} = 488 \text{ nm}$. Adapted with permission from Ref. ⁸. ©2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

ii) Therefore, coated devices with d_{c-c} 's between 356 nm and 506 nm were prepared and subsequently placed in several solvents with increasing refractive index ($RI_{\text{methanol}} = 1.33$, $RI_{\text{ethanol}} = 1.36$, $RI_{\text{butanol}} = 1.40$, $RI_{\text{chloroform}} = 1.45$, and $RI_{\text{toluene}} = 1.50$). The results, depicted in Figure 2.3 (e) – (g) demonstrate the tunability of the SLR position by variation of d_{c-c} and refractive index. By a careful selection of the interparticle spacing, which was tuned by the dwell time of the particles at the interface, and the right solvent (i.e. refractive index) I was able to adjust the SLR in a wavelength range of 161 nm (516 nm – 674 nm) employing a single batch of Ag-PNIPAM particles. Within that range the coupling strength decreased for an increasing d_{c-c} as the spectral overlap between the single particle LSPR and the diffractive mode decreases (depicted example in (e) with $d_{c-c} = 506$ nm in toluene). The influence of the solvent is shown in more detail for a device with $d_{c-c} = 419$ nm in (f). All solvents fully infiltrated the cross-linked PNIPAM coating and when the device was immersed into the different solvents, a stepwise shift of the SLR from 553 – 600 nm was observed. This shift closely followed the (1,0) diffraction mode that shifted from 483 nm to 585 nm as the refractive index of the solvents increased. The experimental results were confirmed by theoretical calculations using the coupled dipole approximation (CDA).

iii) Finally, in order to build devices that allow a dynamic tuning of the SLR wavelength with an easily accessible trigger, I prepared devices with temperature responsive coatings. For this, the PNIPAM coating was only weakly cross-linked by reducing the amount of benzophenone. Like this, the coating exhibited a temperature-dependent swelling and deswelling behavior and a volume phase transition temperature (VPTT) of approximately 32°C when immersed into water. Capitalizing on the change of the RI upon swelling, fully reversible shifts of the SLR position of up to 44 nm were realized, when switching the temperature between 15°C ($RI = 1.33$) and 55°C ($RI = 1.45$) (Figure 2.3 (h)). As the pure polymer possess an RI of 1.52 according to literature⁹ about 36 vol.-% of water is still entrapped into the polymer network. The RI values were determined by fitting theoretical spectra obtained from CDA calculations to the experimentally measured spectra.

2.1.4 In-Plane Surface Lattice and Higher Order Resonances in Self-Assembled Plasmonic Monolayers: From Substrate-Supported to Free-Standing Thin Films

So far, the focus of the optical characterization and manipulation of the self-assembled plasmonic particle arrays was put on the formation and tunability of the SLR. However, this is not the only feature that changes upon variation of certain parameters, like d_{c-c} , particle material and surrounding refractive index environment within the investigated spectral range (300 nm – 1000 nm). Therefore, we extended our model to fully explain the spectral response of plasmonic particle monolayers including higher order resonances. For this, three hexagonally ordered nanoparticle arrays (Ag-PNIPAM: $d_{Ag} = 101 \pm 10$ nm; $d_{c-c} = 503 \pm 27$ nm and $d_{c-c} = 414 \pm 25$ nm; Au-PNIPAM: $d_{Au} = 100 \pm 7$ nm with $d_{c-c} = 510 \pm 24$ nm) were analyzed using AFM and UV-vis absorbance spectroscopy. The arrays were coated repeatedly with NOA 81 via spin-coating and simultaneous UV curing. Each coating step led to an increase of total coating thickness of about 42 nm and between every new step an UV-vis spectrum was measured. As the coating thickness was increased the LSPR of the plasmonic monolayers on glass against air slowly disappeared and instead a SLR was formed at significantly larger wavelength, as depicted in Figure 2.4 (c). Additionally, multiple new features appeared at the lower wavelength side of the SLR (Figure 2.4 (d)). We found, that these features depend on the lattice spacing as well as the coating thickness and can be thoroughly explained with higher order lattice modes.

These new modes follow certain diffraction modes that can be calculated considering the geometry of the particle grating (Figure 2.4 (a), (b)):

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2.1)$$

Here, d is the interplanar spacing, h , k , and l are the Miller indices, a is the in-plane lattice constant (d_{c-c} like for the SLR calculation), and c is the out-of-plane lattice constant with:

$$c = 2(d_{film} - 65 \text{ nm}) \quad (2.2)$$

The diffraction wavelength in dependence of coating thickness and d_{c-c} is then calculated using:

$$\lambda_{hkl} = RI \cdot d \quad (2.3)$$

These diffraction modes can again couple to the LSPR when an overlap between those two features is given and form higher order out-of-plane collective modes. This requirement becomes visible when comparing the thickness-dependent absorbance spectra of the Ag-

PNIPAM array (503 nm; Figure 2.4 (e)) and the Au-PNIPAM array (510 nm; Figure 2.4 (f)). The SLR initially red-shifts to higher wavelengths up to about 300 nm coating thickness. After that, the in-plane surface lattice mode experiences homogeneous refractive index conditions and a further increase of coating thickness hardly influences the SLR. However, the higher order diffraction modes form one after the other and shift to higher wavelengths as the coating thickness increases. As the LSPR region of Au is much more narrow than the one of silver, also the higher order coupled modes are restricted to a smaller wavelength range.

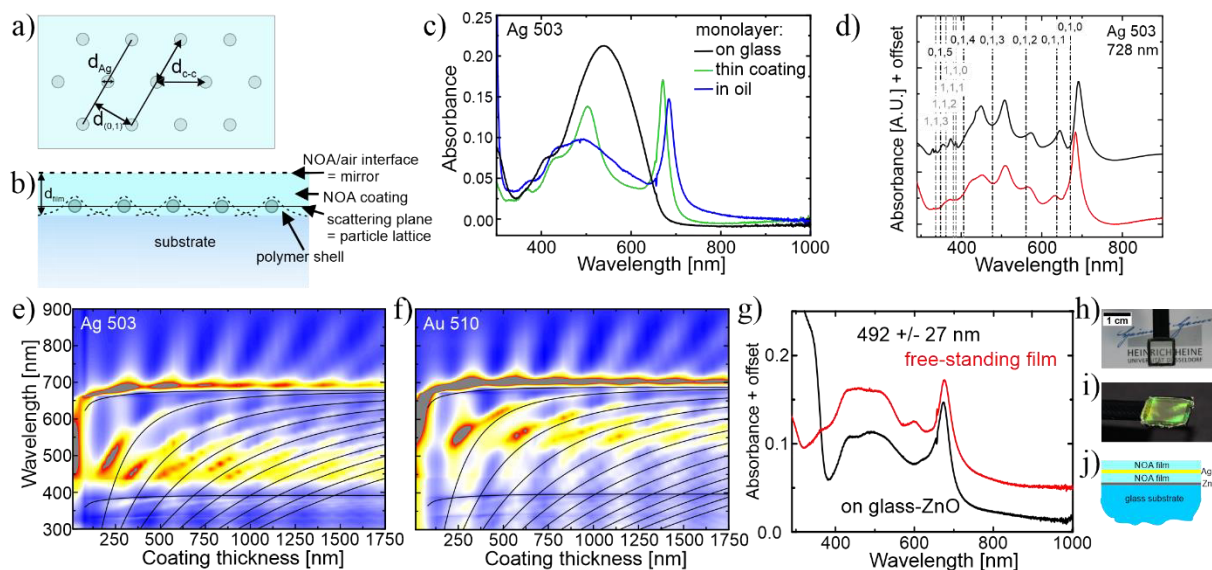


Figure 2.4 In-Plane Surface Lattice and Higher Order Resonances in Self-Assembled Plasmonic Monolayers: From Substrate-Supported to Free-Standing Thin Films. (a) Top-view schematic illustration of hexagonally ordered particle monolayer with d_{c-c} as nearest neighbor center-to-center distance, the silver particle diameter d_{Ag} and $d_{(0,1)}$ the interplanar spacing as an example for the (0,1) group. (b) Side-view sketch of the polymer-embedded (cyan) particle monolayer on glass substrate (blue) illustrating the NOA/air interface acting as a mirror. (c) UV-vis absorbance spectra of hexagonally ordered Ag-PNIPAM monolayer with $d_{c-c} = 503$ nm on glass (black trace), of the same monolayer coated with 224 nm NOA (green trace) and of the coated monolayer additionally covered with immersion oil (blue trace). (d) UV-vis absorbance spectra showing the correlation between 3D diffraction and observed resonances for an Ag-PNIPAM lattice $d_{c-c} = 503$ nm and a NOA coating thickness of approximately 728 nm from experiment (red trace) and from FDTD calculations (black trace). The vertical lines correspond to the calculated Bragg diffraction wavelengths (grey lines: 1,1,x group; black lines 0,1,y group). (e) Absorbance map of Ag-PNIPAM monolayer with $d_{c-c} = 503$ nm and (f) of Au-PNIPAM monolayer with $d_{c-c} = 510$ nm showing the effect of increasing coating thickness on resonance features. The calculated diffraction modes are indicated with black lines. (g) UV-absorbance spectra of Ag-PNIPAM monolayer embedded in NOA on a glass substrate coated with ZnO (black trace, compare sketch in j) and of the same embedded monolayer as free-standing film (red trace). Photographs of the free-standing film supported on a 3D-printed PET frame placed over the university logo (h) in transmission geometry and (i) reflection geometry. Adapted with permission from Ref. ¹⁰. ©2019 American Chemical Society.

Additional to those lattice-related modes, weak dispersive modes can be observed, which solely depend on the film thickness but not on the lattice spacing or the particle material. Therefore, these features can be attributed to thin film interference. Even though the samples were excited under normal incidence in our experiments, angular scattering from the particles enabled this thin film interference.

Lastly, using the fact that approximately 450 nm of polymer matrix are sufficient to support fully developed SLRs, a free-standing plasmonic membrane, exhibiting a SLR, was produced. For this, a NOA₄₅₀/Ag-PNIPAM/NOA₄₅₀ stack was prepared on top of a glass substrate that was previously coated with a thin ZnO layer (Figure 2.4 (j)). This layer served as a sacrificial layer that was etched away via immersion into HCl in the last preparation step in order to detach the NOA₄₅₀/Ag-PNIPAM/NOA₄₅₀ stack from the glass substrate. The final, free-standing structure was collected onto a macroscopic sample holder (0.8 x 0.8 mm²) and had a total thickness below 1 μ m (Figure 2.4 (h), (i)). Most importantly the SLR before and after removal of the glass substrate matched very well with resonances at 676 nm and 673 nm, respectively (Figure 2.4 (g)). This indirectly proved that the NOA films on both sides were sufficiently thick to shield off refractive index influences from the SLR.

2.1.5 Moiré and Honeycomb Lattices through Self-Assembly of Hard-Core/Soft-Shell Microgels: Experiment and Simulation

By depositing more than one particle monolayer, the range of nanostructures available via colloidal self-assembly can be extended. Naturally, the 2D self-assembly at the air/water interface of spherical nanoparticles always leads to the formation of hexagonally close packed arrays. Due to the use of the microgel shell as tunable spacer within these assemblies, I usually prepared structures with well-separated hard (plasmonic) cores. As long as the particle spacing is large enough, the voids between the particles of the first monolayer can be filled in a second deposition step. By careful selection of the monolayer collection and drying conditions well defined honeycomb and Moiré structures were successfully prepared. For both types of structures, the already coated substrate was fully immersed into the water-filled crystallizing dish before the new monolayer was prepared at the air/water interface (Figure 2.5 (a), (b)).

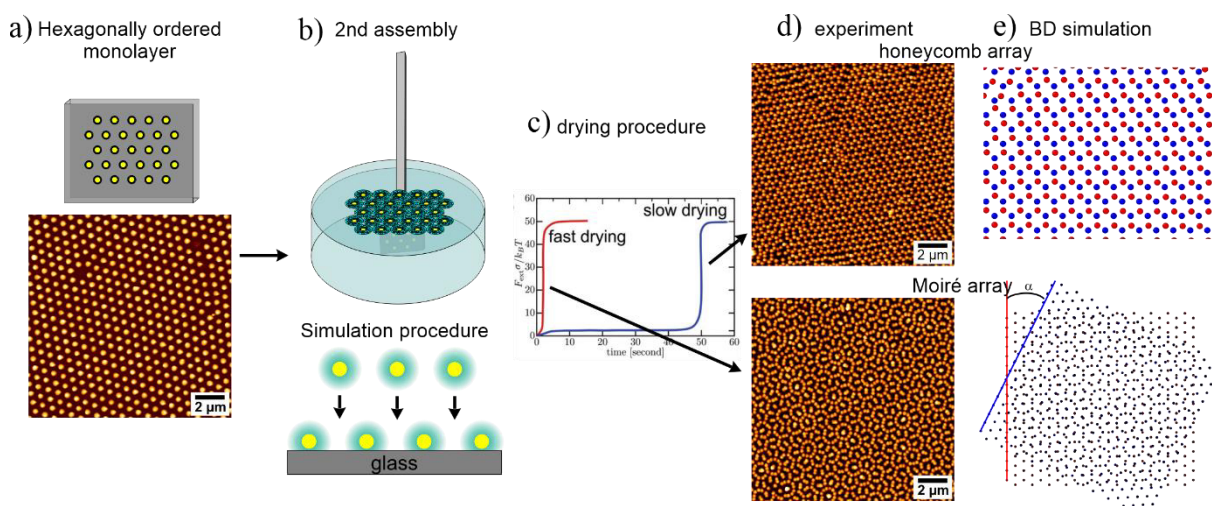


Figure 2.5 Moiré and honeycomb lattices through self-assembly of hard-core/soft-shell microgels. (a) Sketch (top) and AFM height image (bottom) of hexagonally ordered monolayer obtained after first deposition step. (b) Sketch of the 2nd assembly step with the first monolayer submersed vertically in the aqueous phase and the second monolayer floating at the air/water interface (top) and the situation used in Brownian dynamics (BD) simulations. (c) Force profiles applied in BD simulations in order to simulate the fast (red trace) and slow (blue trace) drying procedure. (d) AFM height images of a honeycomb monolayer (top) obtained by slow drying conditions and of a Moiré monolayer (bottom) obtained by fast drying conditions. (e) Honeycomb microstructure (top) and Moiré microstructure (bottom) obtained from BD simulations. α indicates the rotational angle between the first and second deposited monolayer. Adapted with permission from Ref. ¹¹, © The PCCP Owner Societies 2019.

Next, the substrate was slowly retracted through the floating monolayer at a 90° angle in respect to the interface. Thereby, the monolayer attached loosely on top of the first deposited monolayer. Depending on the selected drying conditions, we were able to direct the structure formation. On the one hand, slow drying, in the course of about 5 minutes while the substrate

is left hanging vertically, led to the formation of honeycomb structures. On the other hand, fast drying, within a few seconds led to the formation of Moiré structures (Figure 2.5 (c), (d)).

This behavior can be explained by Brownian dynamics simulations using a flat shoulder potential model. For the slow drying conditions the setup was let to equilibrate for 50 s before a large external force ($F_{\text{ext}} = 50k_B T/\sigma$) was applied, whereas the fast drying condition, i.e. rapid heating, was modelled applying the external force within a couple of seconds (Figure 2.5 (c)). This force, which represents the capillary forces, drives the soft particle shells from the second deposition into the voids of the first monolayer, while the deformation of the particle shells act as a repulsive force. Upon fast drying conditions, the particles from the second deposition are pushed directly into the plane of the first monolayer. Like this, a rotational offset between the first and second monolayer after assembly is maintained during drying and therefore the original structure is frozen in place. Under slow drying conditions, only a small force of $1k_B T/\sigma$ is experienced by the setup during the equilibration phase. This way, the particles of the two layers can interact without overlapping. During this phase a structural transition of the top layer particles, takes place, in which the top layer adapts the configuration of the immobile bottom layer. Thus, regardless of the starting rotational angle after equilibration time a final rotational angle of 2° was observed. In this setting, the application of the large external force ($F_{\text{ext/cap}} = 50k_B T/\sigma$) always leads to the formation of honeycomb structures in the dry sample. Therefore, the formation of Moiré and honeycomb structures under the chosen drying conditions can be reproduced (Figure 2.5 (e)) and explained using Brownian dynamics simulations.

2.1.6 Surface Lattice Resonances in Self-Templated Plasmonic Honeycomb and Moiré Lattices

In this last publication honeycomb and Moiré structures consisting of Ag-PNIPAM ($d_{\text{Ag}} = 101 \pm 10$ nm, $d_{\text{h}(20^\circ\text{C})} = 336$ nm, Au-PNIPAM ($d_{\text{Au}} = 100 \pm 8$ nm, $d_{\text{h}(20^\circ\text{C})} = 336$ nm) and binary lattices, were placed in a homogeneous refractive index environment, in order to study the formation of SLRs in these structures. The arrays were prepared by the double deposition method introduced in the previous chapter and are compared to the SLRs observed in hexagonally ordered arrays, which are obtained after a single deposition. Indeed, distinct SLRs were measured for both, honeycomb and Moiré structures (Figure 2.6 (a) and (c)). I found, that the double deposition process leads to reduced domain sizes in comparison to the hexagonally ordered arrays.

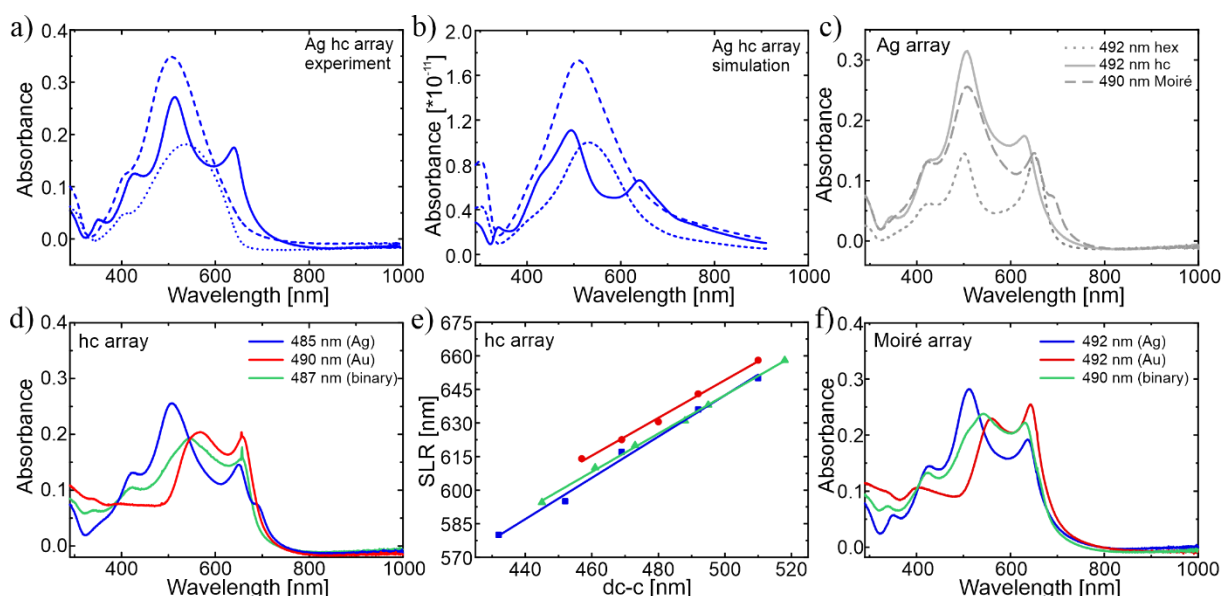


Figure 2.6 Honeycomb and Moiré Lattices and their Surface Lattice Resonances. UV-vis absorbance spectra of a hexagonally ordered silver particle monolayer with $d_{c-c} = 492$ nm on glass (dotted line), a honeycomb monolayer prepared from the hexagonally ordered array (dashed line) and the same honeycomb monolayer coated with a thin PNIPAM layer (blue line) obtained by measurement (a) and by FDTD calculations (b). UV-vis absorbance spectra for (c) the comparison of Ag-PNIPAM monolayer with hexagonally ordered (dotted line), honeycomb (continuous line) and Moiré (dashed line) lattices; (d) honeycomb lattices prepared from Ag-PNIPAM particles (blue trace), Au-PNIPAM particles (red trace) and binary honeycomb structure prepared by depositing an Au-PNIPAM monolayer on top of Ag-PNIPAM monolayer (green trace). (e) SLR wavelength in dependence of d_{c-c} (of the first deposited hexagonally ordered monolayer) for Ag-PNIPAM (blue squares), Au-PNIPAM (red circles) and binary (green triangles) honeycomb monolayers. The lines are linear fits to the data point. (f) UV-vis absorbance spectra of Moiré lattices prepared from Ag-PNIPAM (blue trace), Au-PNIPAM (red trace) and Ag-PNIPAM/Au-PNIPAM (green trace) particles. Adapted with permission from Ref. ¹². © 2021 Wiley-VCH GmbH.

Consequently, this results in a reduced coupling strength and therefore less pronounced SLRs. However, the fact that self-assembled lattices comprising domains with less than 100 particles still show distinct SLRs demonstrates their robustness.

The UV-vis absorbance spectra of the Moiré and honeycomb lattices instead show a larger contribution of the single particle LSPR at shorter wavelength (Figure 2.6 (c)). The shorter wavelength resonance depends on the employed nanoparticle type. Silver nanoparticles show resonance features at approximately 500 nm, whereas gold lattices possess a LSPR at approximately 570 nm. Binary lattices show resonance peaks, that show characteristics of both particle LSPRs resulting in an absorbance maximum at approximately 535 nm (Figure 2.6 (d) and (f)). For the SLR position, the particle material hardly has an influence, because both particle types have a sufficiently large spectral overlap of their respective LSPR with the diffraction mode. Analyzing the SLR wavelengths in honeycomb structures with respect to lattice spacing, the same red-shift of the SLR with increasing d_{c-c} was found for both particle types and the binary lattice. Here the d_{c-c} of the hexagonally ordered sublattice determines the diffraction edge, which results in SLRs for honeycomb and hexagonal lattice with very similar wavelengths (Figure 2.6 (e)). The same is true for Moiré lattices. Also, the rotational angle between the first and second deposited monolayer and therefore the Moiré motif only has a minor influence on the SLR position. All findings were verified using FDTD simulations, nicely matching the experimentally obtained spectra (Figure 2.6 (b)).

2.2 Contributions to Joint Publication

The publications presented in this thesis were prepared in cooperation with colleagues and other research groups. In the following, the individual contributions of all authors are specified in detail.

Chapter 3: Tunable Plasmonic Surfaces via Colloid Assembly

by Tobias Honold, Kirsten Volk, Joseph P.S. Fitzgerald and Matthias Karg

published in *J. Mater. Chem. C* **2015**, 3 (43), 11449-11457. DOI: 10.1039/c5tc02115d

Tobias Honold performed the particle overgrowth with gold of the seed particle dispersion and prepared the monolayers using the Au@Au-PNIPAM particles, characterized the Au@Au-PNIPAM particle dispersions and monolayers using UV-vis absorbance spectroscopy and the monolayers using AFM. He also did the entire characterization using SEM, DLS and zeta potential, carried out the data analysis, prepared the figures, and wrote the manuscript.

I performed the particle overgrowth with silver of the seed particle dispersion, developed the particle assembly process for the core-shell particles and prepared the monolayers consisting of Ag@Au-PNIPAM particles. I characterized the Ag@Au-PNIPAM dispersions and monolayers using UV-vis absorbance spectroscopy as well as the monolayer using AFM, did the data analysis, and corrected the manuscript.

Joseph P.S. Fitzgerald calculated the theoretical extinction spectra via Mie theory and corrected the manuscript.

Matthias Karg synthesized the Au-PNIPAM seed particles, supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

Chapter 4: Time-Controlled Colloidal Superstructures: Long-Range Plasmon Resonance Coupling in Particle Monolayers

by Kirsten Volk, Joseph P.S. Fitzgerald, Markus Retsch and Matthias Karg

published in *Adv. Mater.* **2015**, 27 (45), 7332-7337 DOI: 10.1002/adma.201503672

I developed the concept, synthesized the particles, prepared and characterized the monolayers, did the data analysis, prepared the figures, and wrote the manuscript.

Joseph P.S. Fitzgerald did the theoretical calculations of the particles in dispersion, random monolayers on glass and the hexagonally ordered monolayers. He helped with data interpretation and corrected the manuscript.

Markus Retsch was involved in scientific discussion, prepared the self-assembly sketch, and proofread the manuscript.

Matthias Karg supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

Chapter 5: Reversible Tuning of Visible Wavelength Surface Lattice Resonances in Self-Assembled Hybrid Monolayers

by *Kirsten Volk, Joseph P.S. Fitzgerald, Pia Ruckdeschel, Markus Retsch, Tobias A.F. König and Matthias Karg*

published in *Adv. Opt. Mater.* **2017**, 5 (9), 1600971-1600980. DOI: 10.1002/adom.201600971

I contributed to the concept development, synthesized the particles, prepared the monolayers, polymer coatings, and conducted the UV-vis absorbance and AFM measurements. I did the data analysis, prepared the figures, and wrote the manuscript.

Pia Ruckdeschel took the optical microscopy and SEM images, and proofread the manuscript.

Joseph P. S. Fitzgerald contributed to the concept development, performed the theoretical calculations using the CDA method, was involved in the data analysis and interpretation, was involved in scientific discussion, and corrected the manuscript.

Markus Retsch was involved in scientific discussion, and proofread the manuscript.

Tobias A.F. König performed the theoretical FDTD simulations, calculated the E-field maps, was involved in scientific discussion, and proofread the manuscript.

Matthias Karg supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

Chapter 6: In-Plane Surface Lattice and Higher Order Resonances in Self-Assembled Plasmonic Monolayers: From Substrate-Supported to Free-Standing Thin Films

by *Kirsten Volk, Joseph P.S. Fitzgerald and Matthias Karg*

published in *ACS Appl. Mater. Interf.* **2019**, 11 (17), 16096-16106. DOI: 10.1021/acsami.9b03197

I contributed to the concept development, prepared and characterized all samples, did the FDTD simulations, data analysis and interpretation, prepared the figures, and wrote the manuscript.

Joseph P.S. Fitzgerald set up the initial FDTD simulation setup, was involved in scientific discussion and proofread the manuscript.

Matthias Karg contributed to the concept development, supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

Chapter 7: Moiré and Honeycomb Lattices through Self-Assembly of Hard-Core/Soft-Shell Microgels: Experiment and Simulation

by *Kirsten Volk, Florian Deußenbeck, Suvendu Mandal, Hartmut Löwen and Matthias Karg*

published in *Phys. Chem. Chem. Phys.* **2019**, 21 (35), 19153-19162. DOI: 10.1039/c9cp03116b

I contributed to the concept development, prepared and characterized the monolayers, prepared the figures, and contributed to the manuscript.

Florian Deußenbeck performed the Brownian dynamics simulations, was involved in scientific discussion and proofread the manuscript.

Suvendu Mandal contributed to the concept development, helped with the Brownian dynamics simulation, was involved in scientific discussion, and contributed to the manuscript.

Hartmut Löwen contributed to the concept development, supervised the project, was involved in scientific discussion and corrected the manuscript.

Matthias Karg contributed to the concept development, supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

Chapter 8: Surface Lattice Resonances in Self-Templated Plasmonic Honeycomb and Moiré Lattices

by *Kirsten Volk, Tobias Honold, Déborah Feller and Matthias Karg*

published in *Adv. Mater. Interfaces* **2021**, 8, 2100317-2100325. DOI: 10.1002/admi.202100317

I contributed to the concept development, prepared the monolayers, characterized them using UV-vis absorbance spectroscopy and AFM, analyzed and interpreted the data, did most FDTD simulations, prepared the figures and wrote the manuscript.

Tobias Honold contributed to the concept development, was involved in the preparation of the first monolayers and proofread the manuscript.

Déborah Feller did some FDTD simulations and proofread the manuscript.

Matthias Karg contributed to the concept development, supervised and administered the project, secured funding, provided the necessary infrastructure and reviewed and edited the manuscript.

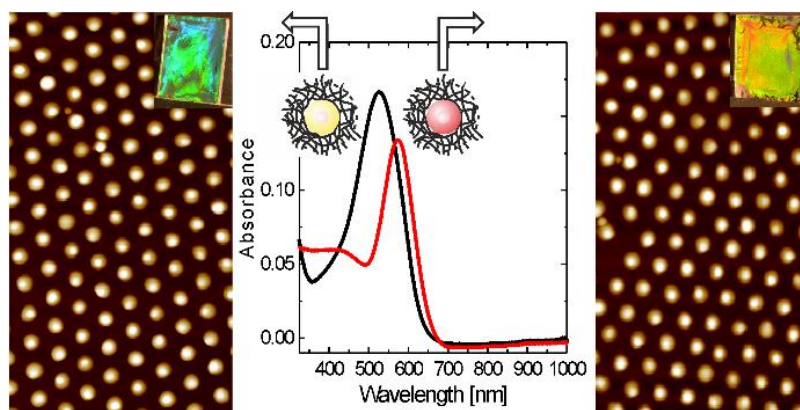
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3 Tunable Plasmonic Surfaces via Colloid Assembly

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Abstract

Self-assembly of plasmonic colloids is a key challenge on the road to the cost-efficient fabrication of optically active surfaces. Here, we show that core-shell particles with plasmonic cores and hydrogel shells are ideal building blocks for coatings with engineered optical properties. The plasmonic properties of the colloids are tuned by selective overgrowth of the gold cores with either gold or silver shells of variable thicknesses. This library of particles is used for monolayer preparation by self-assembly at the air/water interface and subsequent transfer onto solid supports. These monolayers of hexagonally packed particles have very similar particle densities and center-to-center distances, independent of the metal core composition and size. Consequently, our simple and robust bottom-up approach allows us to precisely tailor the optical properties of solid surfaces.

Introduction

Optically functional coatings are critical to materials science with widespread applications in sensing,¹⁻⁷ photovoltaics⁸⁻¹² and metamaterials.¹³⁻¹⁸ Ideal building blocks for such coatings are noble metal nanoparticles due to their ability to support localised surface plasmon resonances (LSPRs).¹⁹⁻²² These LSPRs are collective oscillations of the conduction electrons, causing intense electromagnetic fields in close proximity to the nanoparticle.^{2,23} The plasmon resonance position, width and intensity depend on the particle size, shape and composition, as well as on the refractive index of the surrounding medium.²⁴⁻²⁶ Fortunately, the last several decades have seen tremendous progress in the synthesis of nanoparticles with precise control over these aspects,²⁷⁻³¹ and a broad toolbox of plasmonic particles with tailored resonances is readily available.

Several challenges limit the widespread use of colloidal plasmonic particles in optical devices: Colloidal stability, structural control in assembly, processability, and availability. The first three are primarily the result of an uncontrolled surface chemistry, and the last is due to the low concentrations achievable in most metal nanoparticle synthesis protocols – usually in the nanomolar range. Furthermore, typical reduction protocols yield only particles of a single size and shape population.

A clever way to extend the range of optical properties available through wet-chemical synthesis of plasmonic colloids is the controlled overgrowth of preformed precursor particles. Such seeded-growth protocols allow further tuning of size and shape starting from seed particles.³²⁻³⁴ Through this approach, a library of colloidal building blocks covering a broad range of optical properties (resonance position, width and number of resonances) is accessible.

In this work, we propose core-shell colloids with small, spherical gold cores and semi-transparent hydrogel shells as a convenient precursor material for seeded-growth and the realisation of plasmonic surfaces with tailored optical properties. The hydrogel encapsulation was realised by seeded precipitation copolymerisation of N-isopropylacrylamide (NIPAM) and N,N-methylenebisacrylamide (BIS) according to a well-established protocol.³⁵ The role of the hydrogel shell is threefold: 1) To ensure colloidal stability in aqueous dispersion and different organic solvents such as alcohols. 2) To control surface coverage upon assembly of the particles into, e.g., a monolayer.³⁶ 3) To allow for diffusion-controlled overgrowth of the gold nanoparticle cores.³⁷⁻³⁹

We employed this strategy to generate a library of plasmonic core-shell particles with the same hydrogel shell and hydrodynamic diameter but with different plasmonic metal cores. Our synthetic protocol allows us to adjust precisely the absorbance and the LSPR position of our particles within a range of wavelengths as large as 100 nm. This is confirmed by simple Mie theory calculations. These particles were assembled at the air/water interface and subsequently transferred onto glass slides. The particle density and the hexagonal packing of the transferred particle arrays are found to be independent of the size and composition of the plasmonic cores. The particle packing is solely determined by the hydrogel shell. Consequently, monolayers with very similar particle densities but significantly different absorption/scattering ratios and LSPR peak wavelength were prepared. Such structures are easily fabricated in a fast, cost-efficient and reproducible manner on cm-scale substrates. Upscaling to larger sample sizes may become possible in a role-to-roll production approach.⁴⁰ Our plasmonic coatings are particularly interesting as light management structures in hybrid photovoltaic devices.⁸

Experimental Section

Chemicals

Ascorbic acid (Aldrich, >99%), 3-butenylamine hydrochloride (Aldrich, 97%), cetyltrimethylammonium bromide (Aldrich, CTAB, >98%), cetyltrimethylammonium chloride (CTAC, Aldrich, 25 wt. %, H₂O), ethanol (abs. VWR), glycine (Merck, > 99.7 %), H₂O₂ (VWR, 30%), N-Isopropylacrylamide (Aldrich, 97%), N,N'-methylenebis(acrylamide) (Aldrich, 99%), NH₄OH_{aq} (Applichem, 25%), potassium peroxodisulfate (Merck, 99%), silver nitrate (Fluka, >99.5%), sodium dodecylsulfate (SDS, SERVA, 99%) and tetrachloroauric(III) acid (Aldrich, 99.999%) were used as received. Milli-Q water with a resistivity of 18.2 MΩ · cm was used in all synthesis and purification procedures.

Synthesis

Precursor particles. The precursor particles were prepared following a previously published protocol.³⁵ In brief, citrate stabilised gold nanoparticles of approximately 20 nm in diameter were prepared according to the Turkevich method⁴¹ and functionalised by the addition of butenylamine hydrochloride. The particles were purified and concentrated by centrifugation. The functionalised gold nanoparticles were encapsulated by hydrogel shells using a seeded precipitation polymerisation of N-Isopropylacrylamide (0.06 M) and N,N-methylenebisacrylamide (15 mol-% as referred to monomer) as cross-linker. The polymerisation was carried out at 70°C for two hours. The core-shell particles were then purified by centrifugation and redispersion in water. The final purified product was freeze-dried.

Gold overgrowth. Au@Au-PNIPAM particles were obtained by using a modified surfactant assisted seeded-growth protocol in order to overgrow the gold nanoparticle cores of the precursor particles.³² All overgrowth experiments were done using a constant molar ratio of ascorbic acid/HAuCl₄ of 1.3. At first, a precursor stock solution was prepared by diluting a 2 wt.% solution of precursor particles with the same volume of a 100 mM CTAC solution. Next, a feed solution was prepared containing 0.5 mM HAuCl₄ and 4.75 mM CTAC. In a typical synthesis, 200 µL precursor stock solution was combined with 8 mL of a 2.4 mM CTAC solution under heavy stirring in a 20 mL glass vial, followed by the addition of 83 µL of a freshly prepared ascorbic acid solution (10 mM). Next, 1.280 mL feed solution was added dropwise to the seed solution under stirring. The reaction was allowed to proceed for 20 minutes. The particles were purified by centrifugation at 3740 rcf until the supernatant was colourless. The supernatant was discarded and the precipitate was redispersed in water. This process was repeated twice. The final core size of the particles was 30 nm as determined by transmission electron microscopy (TEM). Particles with overgrown gold cores of 41, 60 and 92 nm in diameter were obtained by adding 3.0, 6.7 and 29.3 ml feed solution to the precursor particles, respectively.

Silver overgrowth. Similar to the gold overgrowth, Ag@Au-PNIPAM particles were synthesised following a surfactant assisted protocol for overgrowth of the initial gold cores of the precursor particles with silver.⁴² In a typical synthesis, 2.860 mL precursor particles were added to 10 mL of a 50 mM CTAB solution containing 400 mM glycine under heavy stirring. Next, 800 µl of a 0.1 M NaOH and 450 µL of a 100 mM freshly prepared ascorbic acid solution were added to the precursor particles. 1.31 mL of a 15 mM AgNO₃ feed solution was added dropwise to the seed solution and stirring was continued for 20 min. The particles were purified

as described above. The final core size was 28 nm as determined by TEM. Larger cores were obtained by reducing the volume of precursor particles to 800 μL (46 nm cores), 146 μL (72.7 nm cores) and 50 μL (99.8 nm cores), respectively.

Monolayer preparation

Cleaning of glass slides. Microscope slides (Thermo Scientific) were cleaned by sonication in acetone, 2-propanol and water for 20 min each, followed by heating at 80°C in a 1:1:5 mixture by volume of H_2O_2 , $\text{NH}_4\text{OH}_{\text{aq}}$ (25%) and H_2O for 30 min. Afterwards, the glass slides were cleaned with water several times and dried using nitrogen gas.

Assembly. All core-shell particles were assembled into monolayers at the air/water interface using a crystallising dish filled with a dilute, aqueous SDS solution (0.05 mM).⁴³ A clean glass slide was placed inside the crystallising dish at a tilt angle of approximately 30°. A concentrated particle dispersion was transferred into an Eppendorf tube, diluted with the same volume of EtOH and homogenised using a Vortexer. 0.1-0.2 mL of the dispersion were filled into a 1 mL syringe equipped with a 27G $\times$ 3/4" cannula (0.4 $\times$ 20 mm). The water/ethanol solvent mixture was chosen in order to allow for spreading of the particle dispersion at the air/water interface. SDS was used below the critical micelle concentration. The surfactant acts as a soft blocking layer and facilitates the transfer of the monolayer on a solid support.⁴⁴ We adjusted the bulk concentrations of the particle dispersions between 1 and 2 wt.%, depending on the size of the plasmonic core of the particles. The particle dispersion was steadily transferred via the glass slide onto the air/water interface, forming a freely floating monolayer. The monolayers were collected onto 1 cm² glass substrates. The substrates were immersed below the monolayer and withdrawn at a shallow angle, lifting out the floating particle monolayer. Immediately after withdrawal of the monolayer, the samples were carefully dried using a heat gun.

Characterisation

TEM. All core-shell particles were analysed by transmission electron microscopy (TEM) using a ZEISS CEM 902 TEM operating at an acceleration voltage of 80 kV. Samples were prepared by drop casting of strongly dilute, aqueous particle dispersions on carbon coated copper grids (200 mesh). The dried samples were investigated in bright-field operation. Image analysis was done with the image processing software ImageJ, measuring the size of at least 100 different particles (metal cores) for each sample.

AFM. 10 $\times$ 10 μm^2 AFM images were recorded with a Nanoscope Multimode AFM (Veeco) in tapping mode. The particle monolayer on glass substrates were measured at ambient conditions in air. OTESPA-R3 AFM probes (Bruker) with spring constant of approximately 26 N/m were

employed. Only the height profiles were used for image analysis. All images were flattened (1st order) using the Nanoscope (Bruker) software. Nearest neighbour center-to-center distances were obtained using ImageJ.

SEM. The particle monolayers were investigated using scanning electron microscopy (SEM) with a ZEISS Ultra plus field emission scanning electron microscope (FE-SEM). The samples were vapour coated with approximately 30 nm of carbon using a Balzers Union MED 010 device. Images were recorded with an acceleration voltage between 2-10 kV using an in-lens and a SE2 detector to visualize the topography of the sample.

DLS and zeta potential. Dynamic light scattering (DLS) and zeta potential (ζ) experiments were performed on a NanoZS Zetasizer (Malvern Instruments) equipped with a 633 nm He-Ne laser at a detection angle of 173° . For all core-shell samples, dilute aqueous dispersions were measured at 25°C . The samples were equilibrated for 10 minutes before acquisition of the correlation functions. For DLS experiments, three correlation functions were recorded for each sample using acquisition times of 60 seconds. The hydrodynamic diameter were obtained by Cumulant analysis provided by the instrument software. Electrophoretic mobilities were measured and calculated into ζ -potentials by the instrument software using the Einstein-Smoluchowski relation. Three consecutive measurements were performed for each sample.

UV-Vis extinction spectroscopy. All absorbance spectra were measured in a wavelength range of 190 – 1100 nm using an Agilent 8453 UV-Vis Spectrophotometer. Dilute aqueous dispersions of the core-shell particles were measured in quartz cells with 1 cm light path. Spectra of the particle monolayers were recorded using glass substrates as solid supports. All experiments were performed at ambient conditions.

Calculation of theoretical extinction spectra. Theoretical extinction spectra were calculated via Mie theory using Mathematica 10, following the multilayer recursive method.⁴⁵ Particle core dimensions were taken from TEM measurements, with a hydrogel shell diameter of 330 nm. Overgrown particles include a 20-nm-diameter gold core. The refractive indices of gold and silver were taken from Johnson and Christy⁴⁶ and modified to include electron surface scattering at small sizes.⁴⁷ The refractive index of the hydrogel shell was given by a simple model of $n_{\text{H}_2\text{O}} + dn$, where $n_{\text{H}_2\text{O}}$ is the refractive index of water,⁴⁸ and $dn = 0.05$ was the best fit value to the precursor particle absorption spectra. The host medium was water. Multipole expansions included 5 – 8 terms, such that all calculated wavelengths have less than 0.1% relative error.

Results and Discussion

Au-PNIPAM precursor particles

To address the challenges of colloidal stability and control of particle-particle separation, we encapsulated plasmonic gold nanoparticles with rather thick hydrogel shells. This shelling procedure is based on a seeded precipitation polymerisation protocol.³⁵ The obtained core-shell precursor particles (Au-PNIPAM) have single gold nanoparticle cores of 20 nm in diameter as obtained by TEM and soft, cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) shells. The overall hydrodynamic diameter of the core-shell particles dispersed in water is 325 nm as determined by DLS (25°C, swollen state). Consequently, the swollen shell has a thickness on the order of 150 nm. The porous, highly swollen structure of the hydrogel allows diffusion of small molecules into the shell, so post-modification of the gold core is possible.

Overgrowth of the cores of the precursor particles

In order to achieve a whole toolbox of core-shell particles with different plasmonic properties but the same overall particle dimensions and interactions, we applied successive overgrowth of the precursor cores by gold and silver. This way we changed the diameter and composition of the cores starting from only one precursor system (Au-PNIPAM).

We used surfactant assisted seeded-growth protocols in combination with mild reducing conditions to guarantee homogeneous overgrowth of the gold precursor cores and suppress secondary nucleation. Previous studies have shown that the ratio of reactants, pH, temperature, concentration of the surfactant, and nature of the halide counter ion strongly influence the final nanoparticle morphology.^{49, 50} The surfactant cetyltrimethylammonium chloride (CTAC) was chosen for the gold overgrowth because it helps to suppress the formation of non-spherical geometries. Due to the presence of the surfactant, the redox potential of the metal salt is changed through complexation. Consequently, complete reduction takes place only at the metal surface when a mild reducing agent is used.⁵¹ Control on the core size was achieved by adding increasing amounts of feed solution and the reducing agent ascorbic acid to the precursor particles. A similar protocol was used for the silver overgrowth, which was done under basic conditions (pH approx. 10) in order to increase the reducing strength of ascorbic acid.⁵² The synthetic protocol was adjusted in order to get similar core sizes as for the Au@Au-PNIPAM particles by variation of the amount of seed particles.

The core-shell particles upon successive overgrowth of the precursor cores will be denoted Aux@Au20-PNIPAM and Ag_y@Au20-PNIPAM throughout the rest of the manuscript. Here *x* (*y*) refers to the thickness of the gold (silver) shell, and Au20 refers to the initial gold core of 20 nm in diameter. For instance, Ag₄@Au20-PNIPAM is a core-shell system with a 4-nm-thick

silver shell, grown on the gold core with 20 nm in diameter. Therefore, the total core diameter of this example particle is 28 nm.

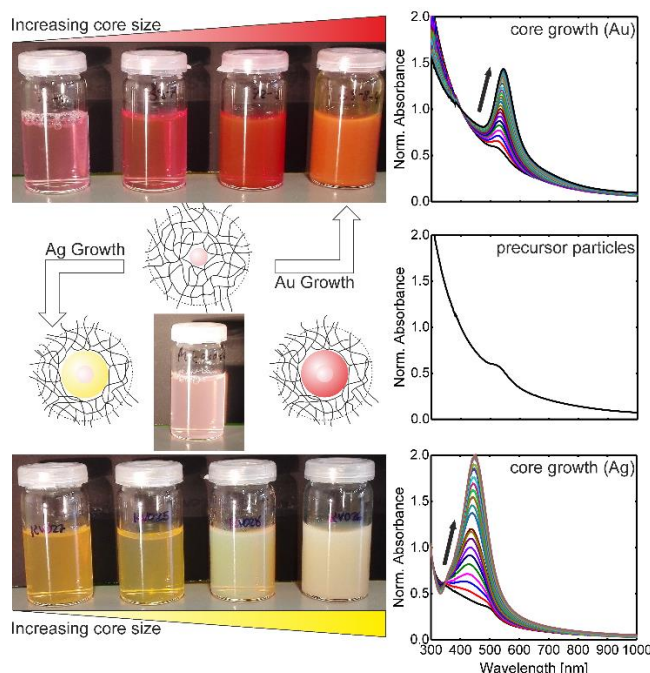


Figure 1. Controlled overgrowth: The gold core of the initial core-shell particles, Au-PNIPAM, with gold cores of 20 nm in diameter (left column, middle) can be selectively overgrown with silver (bottom) or with gold (top) leading to an increase in core size. The respective absorbance spectra (right column) illustrate the changes of the optical properties during the overgrowth with silver (bottom) and with gold (top). The spectra were normalized to the absorbance at 400 nm (gold overgrowth) and at 300 nm (silver overgrowth).

Figure 1 shows schematic depictions of the structure of the different kinds of core-shell particles along with photographs of samples before overgrowth (Au-PNIPAM) and after progressive steps of gold growth (Au@Au-PNIPAM) as well as silver growth (Ag@Au-PNIPAM). The change in core size is clearly visible from the photographs. While the precursor particles appear as a slightly red and turbid dispersion, the overgrown samples exhibit much stronger colour: red for gold and yellow for silver. This increase in colour intensity is related to the increasing absorption of the cores with larger sizes. At the same time, the photographs of the particle dispersions show that the scattering of the samples increases with the core size. This is the result of the increased scattering cross-section for the larger cores.

The optical impression from the photographs of the samples is confirmed by UV-Vis absorbance spectra shown in the right column of Fig. 1. The spectrum in the middle of the right column represents the absorbance of the precursor particles, Au-PNIPAM. The spectrum reveals a weak LSPR peak, originating from the gold cores, at approximately 523 nm. The

strong scattering of the relatively large hydrogel shell dominates the spectrum. This is visible as an increase in absorbance for shorter wavelengths.³⁵

The changes of the optical properties for the overgrown samples are entirely attributed to the scattering and absorption of the plasmonic cores because the hydrogel shell dimensions will be nearly unaffected by the core growth (see hydrodynamic diameter D_h in Table 1). When the precursor particles are overgrown, the absorption to scattering ratio changes, and the plasmonic properties become more pronounced (Fig. 1, right column, top and bottom). For both growth materials, Au and Ag, the plasmon resonance intensifies with increasing core size. Furthermore, the position of the plasmon resonance is affected by the overgrowth of the metal cores: For gold as growth material, a continuous shift of the plasmon resonance to longer wavelengths is observed for increasing core dimensions. For growth with silver, the plasmon resonance initially shifts to shorter wavelengths as compared to the initial Au-PNIPAM precursor particles. This is caused by the higher restoring force from the nuclei in silver as compared to gold. Upon growth of the silver shell the plasmon resonance shifts to longer wavelengths as the thickness of the silver shell increases. In order to better understand this transition, we synthesised four different metal shell thicknesses using gold and silver growth each aiming at comparable shell thicknesses for the two metals.

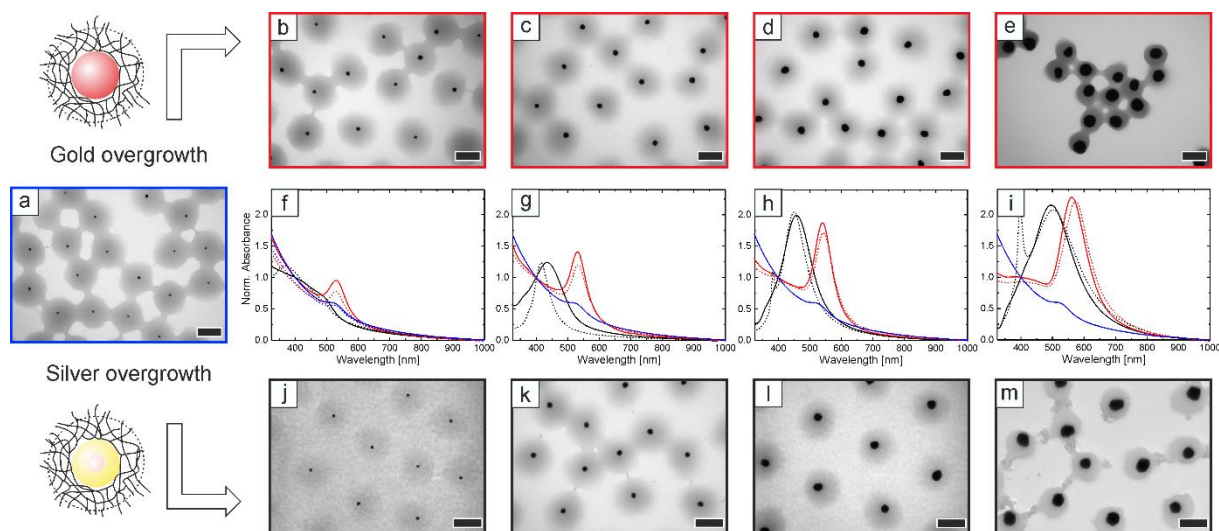


Figure 2. Microscopic and spectroscopic characterization of the plasmonic particles after different steps of core growth. a: TEM image of the initial precursor particles, Au-PNIPAM. b – e: TEM micrographs after overgrowth with gold. j – m: TEM micrographs after overgrowth with silver. All scale bars in the TEM images correspond to 100 nm. The average core diameters of the Au@Au-PNIPAM particles are 30 nm (b), 41 nm (c), 60 nm (d) and 92 nm (e) and 28 nm (j), 46 nm (k), 73 nm (l), and 100 nm (m) for Ag@Au-PNIPAM. f – i: UV-Vis absorbance spectra for the precursor particles (blue solid lines), the Au@Au-PNIPAM particles (red solid lines) and the Ag@Au-PNIPAM particles (black solid lines). Spectra for similar overall core sizes after overgrowth with gold and

silver were plotted in one diagram for comparison. The dashed lines are theoretically calculated extinction spectra obtained by Mie theory.

Figure 2 shows TEM images of the whole set of synthesised particles, including the precursor particles (a). The spherical gold nanoparticles of the precursor particles are clearly visible as circles of much higher contrast (black) as compared to the PNIPAM-shell (grey). Note that each precursor particle contains only one gold core. The TEM micrographs in Fig. 2 b – e show the particles after overgrowth with gold. The diameter of the spherical cores is clearly increasing from (b) to (e). This way, gold shell thicknesses between 5 and 36 nm are accessible, corresponding to total core sizes of 30 to 92 nm. This range of sizes is significantly larger as compared to the ones realized in a previous work where we performed overgrowth of already adsorbed particles (monolayer by spin-coating).³⁷ Furthermore, much better control on the particle morphology upon overgrowth was achieved in the present work. Non-spherical side products and secondary nucleation were not observed. Similar overgrowth results were obtained with silver, as can be seen by the TEM micrographs j – m in Fig. 2. Spherical particles with silver shell thicknesses of 4 to 40 nm closely match the results of the gold overgrowth. The core dimensions from TEM analysis are listed in Table 1.

Table 1. Summary of the different plasmonic colloids prepared from core overgrowth of Au-PNIPAM precursor particles. The average core diameter D_{core} was obtained from size analysis of the TEM micrographs. $\lambda_{\text{LSPR(Exp)}}$ denotes the position of the LSPR obtained from the UV-vis measurements of aqueous particle dispersions and $\lambda_{\text{LSPR(Mie)}}$ gives the LSPR position obtained from Mie calculation. D_h is the hydrodynamic diameter of the particles and ζ denotes the zeta potential, both measured in water at 25°C.

Sample	D_{core} [nm]	$\lambda_{\text{LSPR(Exp)}}$ [nm]	$\lambda_{\text{LSPR(Mie)}}$ [nm]	D_h [nm]	ζ [mV]
Au-PNIPAM	20±2	523	530	325	-17.3
Au5@Au20-PNIPAM	30±4	532	532	325	-17.3
Au10@Au20-PNIPAM	41±5	532	531	315	-2.9
Au20@Au20-PNIPAM	60±7	540	541	316	-4.2
Au36@Au20-PNIPAM	92±12	561	568	316	-1.1
Ag4@Au20-PNIPAM	28±3	-	380	336	-11.5
Ag13@Au20-PNIPAM	46±3	433	437	317	-6.8
Ag26@Au20-PNIPAM	73±5	458	464	329	-9.3
Ag40@Au20-PNIPAM	100±6	496	503	336	-9.6

The ensemble absorbance spectra of the Au@Au-PNIPAM and Ag@Au-PNIPAM particles in aqueous dispersion are plotted in Fig. 2 f – i. For comparison, spectra of Au@Au-PNIPAM and Ag@Au-PNIPAM colloids of similar core sizes are plotted in the same graphs along with theoretical extinction spectra. Additionally, the absorbance of the Au-PNIPAM precursor particles is included in each graph (blue solid lines). The spectra are normalised to the absorbance at 400 nm for an easier comparison. Almost all samples show a pronounced, single

extinction peak that is attributed to the dipolar LSPR of the metal cores, with the exception of the precursor and the smallest overgrown silver particles. The small half width of the resonances manifests the low polydispersity of our particles despite several steps of sequential overgrowth. The absence of any other plasmonic modes further highlights that the core overgrowth did not produce any non-spherical particle morphologies as side products.

Having a closer look at the LSPR peak positions, a change from 523 to 561 nm is observed for gold as growth material. The resonance red shifts and the absorbance at the resonance increases with increasing core size. For silver as growth material a slightly different behaviour is observed for the first step of core growth. Overgrowth with a 4-nm-thick silver shell broadens and blue shifts the local absorbance maximum as compared to the LSPR of the initial Au-PNIPAM colloids. A clear LSPR peak cannot be clearly determined. This can be attributed to a synergistic effect between the two metals, where the gold core induces significant damping due to the mismatch of the dielectric function of the bimetallic core.⁵³ Increasing the silver shell further to 13 nm leads to a significant change of the optical properties and a clear LSPR peak is now detectable. This LSPR is significantly blue shifted (by 90 nm) as compared to the Au-PNIPAM particles. For these particles, the bimetallic cores behave optically very similar to pure silver spheres due to the low volume fraction of the gold core (8%) and shallow skin depth of the surface plasmon. With a further increase in the silver shell thickness, the LSPR shifts to longer wavelength and becomes more intense. The LSPR positions of all particles with Ag@Au cores lie in a range of 433 – 496 nm. The LSPR wavelengths, λ_{LSPR} , of all samples are summarised in Table 1. The observed peak wavelengths of the resonances agree well with results from literature.³²

Theoretical extinction spectra of spherical particles with core dimensions from TEM analysis are included in Fig. 2 as dotted lines. A very good match between the experimental and the calculated spectra is found for all core-shell particles with gold cores, including the Au-PNIPAM precursor particles. Table 1 shows that both sets of spectra provide nearly identical positions of the LSPR maximum, except for Au36@Au20-PNIPAM. In the latter case, small deviations of the spherical shape of these particles could explain the difference between the two LSPR positions. Simulations of Ag26@Au20-PNIPAM and Ag40@Au20-PNIPAM particles also match closely to the ensemble spectra. However, the simulated quadrupolar mode at 382 nm (Ag26@Au20-PNIPAM) and at 398 nm (Ag40@Au20-PNIPAM) is not observable in the experimental spectra. We attribute this to an irregular morphology of the silver shell in the overgrown particles. In figure 2 m, the faceted character of the polycrystalline particles explains the deviation of the simulated spectra, which assume an ideal spherical geometry of

the nanoparticles. In the case of Ag13@Au20-PNIPAM, simulation and experimental spectra differ significantly. An anisotropic growth of the silver shell or slight variation of core sizes could explain the observed deviations, which are even more pronounced for the Ag4@Au20-PNIPAM particles. We attribute this to the synergistic effect of the gold and silver as discussed above.

Plasmonic monolayer via colloidal assembly

In the next step, we used our library of core-shell colloids for the assembly into ordered monolayers. Our particles are mostly stabilised by steric interactions. The surface charge, stemming from the anionic radical initiator used in the shell growth, is small and slightly negative. Zeta potentials measured in aqueous dispersion at 25°C reveal only small changes of the surface charge when the core size is changed (see Table 1) which might be a result of incomplete removal of CTAB used in the core growth. Thus, we expect very similar particle-particle interactions for the whole series of particles independent of the core dimensions. For the assembly, particle dispersions in a 1:1 mixture (by volume) of H₂O and ethanol were floated at the air/water interface, as described in the Experimental Section.⁴³ However, we want to stress here the freely floating monolayer did not cover the whole accessible surface area of the air/water interface, which is rather different as compared to typical interface assemblies as realized in, e.g., a Langmuir trough. After immersing the particles at the interface, the spontaneously formed monolayers were transferred onto glass substrates by gentle lifting. Upon transfer onto glass slides, the monolayers were investigated by AFM and UV-Vis spectroscopy. AFM images were always recorded with different scan sizes and at completely independent, random sample positions. We did not find any significant deviation on the degree of order nor on the inter-particle distances at different sample positions.

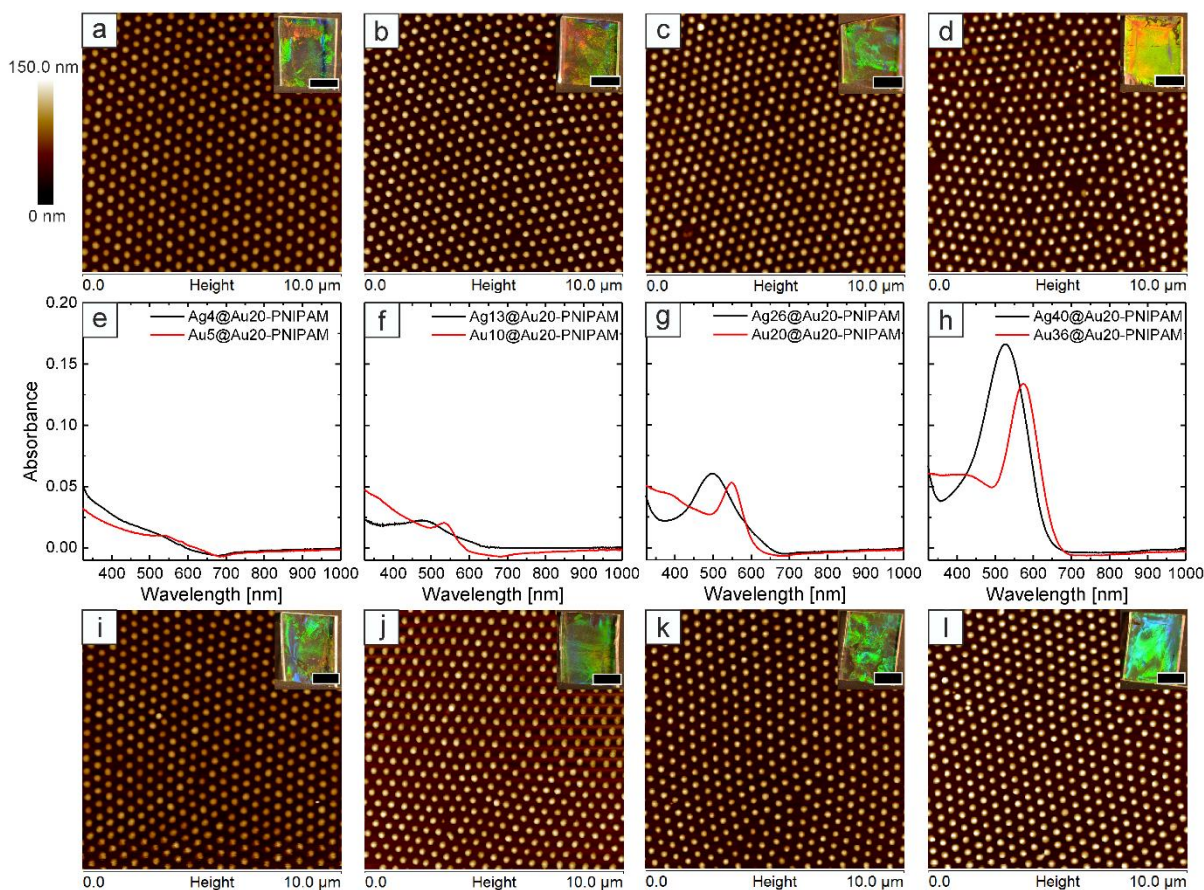


Figure 3. Characterization of Au@Au-PNIPAM and Ag@Au-PNIPAM monolayers. a – d: Tapping mode AFM height profiles of Au@Au-PNIPAM particles. e – h: UV-Vis spectra of the monolayers on glass. Spectra of Au@Au-PNIPAM and Ag@Au-PNIPAM arrays with comparable core sizes are combined in one graph (a&i, b&j, c&k and d&l.) i – l: AFM height profiles of Ag@Au-PNIPAM arrays. The insets show digital photographs of the monolayers on glass slides of approximately 1 cm^2 . The scale bars correspond to 5 mm.

Representative results from these measurements are presented in Fig. 3. SEM images of the monolayers a-d and i-l are provided in the supporting information, figure S1-S8. Images a – d show selected 10x10 μm^2 AFM height profiles of Au@Au-PNIPAM arrays on glass, and similarly i – l the profiles of Ag@Au-PNIPAM arrays. Additionally, digital photographs of the particle monolayers on glass slides of approximately 1 cm^2 are included as insets in Fig. 3 a – d and i – l. The photographs show homogeneous coverage over the whole substrates as evident from the strong iridescence colours. As can be seen from the AFM images, all particles assembled into highly ordered, hexagonally packed monolayers. Large ordered domains are observable. Furthermore, a clear separation between the particles is found. This is related to the shrinkage of the previously highly swollen hydrogel shell upon drying of the monolayer. The particle density and nearest neighbour distance d_{c-c} of the monolayers are summarised in Table 2.

Table 2. Analysis of particle monolayers. Center-to-center distances (d_{c-c}) and particle densities (ρ) were obtained from the AFM height profiles using ImageJ software. The LSPR positions (λ_{LSPR}) and absorbance values ($Abs(\lambda_{LSPR})$) were extracted from absorbance spectra of monolayers on glass

Sample	d_{c-c} [nm]	ρ [particles/ μm^2]	λ_{LSPR} [nm]	$Abs(\lambda_{LSPR})$
Au5@Au20-PNIPAM	473 ± 15	4.49	-	-
Au10@Au20-PNIPAM	465 ± 14	4.76	536	0.02
Au20@Au20-PNIPAM	445 ± 15	4.94	547	0.053
Au36@Au20-PNIPAM	463 ± 19	4.45	573	0.133
Ag4@Au20-PNIPAM	461 ± 23	4.71	-	-
Ag13@Au20-PNIPAM	455 ± 22	4.77	484	0.022
Ag26@Au20-PNIPAM	453 ± 23	4.48	499	0.06
Ag40@Au20-PNIPAM	459 ± 20	4.67	527	0.166
binary sample	455 ± 17	4.67	564	0.146

All monolayers have comparable particle densities with an average of 4.65 particles/ μm^2 and values of d_{c-c} in the order of 460 nm. The inter-particle distance is large compared to the average hydrodynamic diameter of 323 nm of the particles measured with DLS (Table 2). This points to an anisotropic deformation the hydrogel shell at the interface as has been observed previously for purely organic hydrogel particles adsorbed at a liquid/liquid interface.⁵⁴ Since all monolayers show very similar values of d_{c-c} and very regular, hexagonal packing of the particles independent on the size and composition of the plasmonic metal core, it is obvious that only the hydrogel shell drives the particle assembly. In other words, interface assembly of our metal-hydrogel core-shell particles allows the fabrication of highly ordered monolayers with nearly the same surface coverage from Au@Au and Ag@Au nanoparticles covering a diameter range from 20 to 100 nm. Because the monolayer structure and density is nearly the same for all samples, we can now investigate the dependence of the optical properties on the core size and material using far-field extinction spectroscopy.

Figure 3 e – h show UV-Vis extinction spectra of the monolayers on glass. For comparison, the absorbance of Ag@Au-PNIPAM and Au@Au-PNIPAM monolayers with comparable sized cores are plotted in one graph. The spectra show very similar results as compared to those recorded in solution (Fig. 2). It is worth noting that the illuminated area on the substrates is the same for all samples and that the spectra shown in Fig. 3 were not normalised nor shifted. Therefore, we conclude that the increase in absorbance is solely related to the increasing core volume, since roughly the same number of particles is probed for each sample.

The determined LSPR peak positions and values of absorbance at the resonance are listed in Table 2. For the smallest core sizes (Fig. 3 e) the weak LSPR signal is related to the small

absorption and scattering cross-sections of these rather small metal nanoparticle cores. With increasing core size, the plasmonic properties of the samples become more pronounced.

Figure 4 a shows the dependence of the LSPR position (λ_{LSPR}) as a function of the metal shell thickness obtained after each step of core growth, both of the particles in solution and of the monolayers on glass. Because of the high sensitivity of the plasmon resonance to the local refractive index, the peak positions of the particle monolayers on glass are shifted to longer wavelengths for both types of particles.²⁶ This effect is stronger for the cores overgrown with silver. Furthermore, Fig. 4 b shows that the absorbance of the different monolayers increases with the plasmonic shell thickness of the overgrown cores, independent of the growth material, i.e., silver and gold. For both sets of samples, the maximum shell thicknesses exhibit an absorbance increase by almost a factor of 10. This nicely underlines that our colloidal library not only allows the fabrication of plasmonic coatings with tailored resonance positions but also the tuning of the absorbance and consequently transmission of the monolayer.

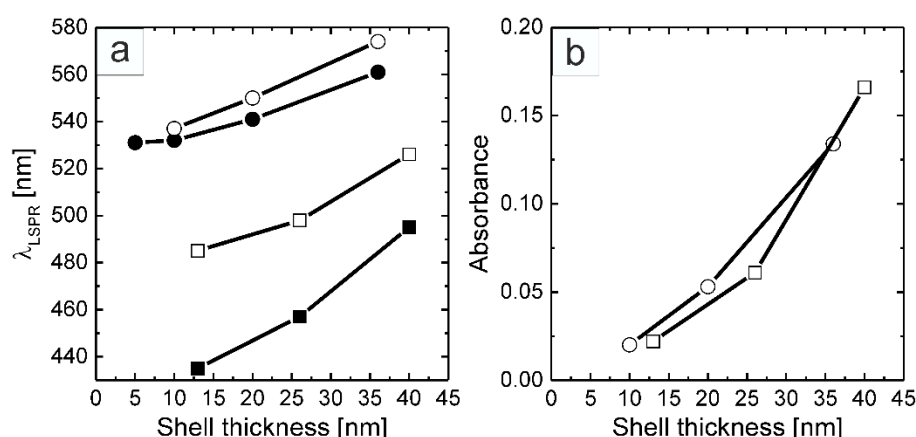


Figure 4. Results from analysis of the UV-Vis absorbance spectra. a: LSPR peak wavelength, λ_{LSPR} , and b: absorbance at the LSPR maximum as a function of the shell thickness obtained after sequential overgrowth of the gold cores of the precursor particles. Results are shown for spectra measured from aqueous dispersions (filled symbols) and monolayers on glass (open symbols) and for Au@Au-PNIPAM (circles), and Ag@Au-PNIPAM (squares).

Mixed monolayer

To further demonstrate the tunability of the optical properties of our self-assembled particle arrays, we prepared a 1:1 mixed monolayer (by weight) of Ag40@Au20-PNIPAM and Au36@Au20-PNIPAM particles. Figure 5 a and b show an AFM height profile and a FE-SEM image of the binary monolayer, respectively. The images indicate homogeneous surface coverage and an ordered packing of the particles, very similar to the monolayers of single core species shown in Fig. 3. The average particle center-to-center distance of 452 ± 19 nm is similar to the previously discussed monolayers. Due to their same hydrodynamic dimensions (see Table

1) and hydrogel shell morphology, particles assemble into ordered structures with inter-particle distances and order parameters independent of the plasmonic core size and composition.

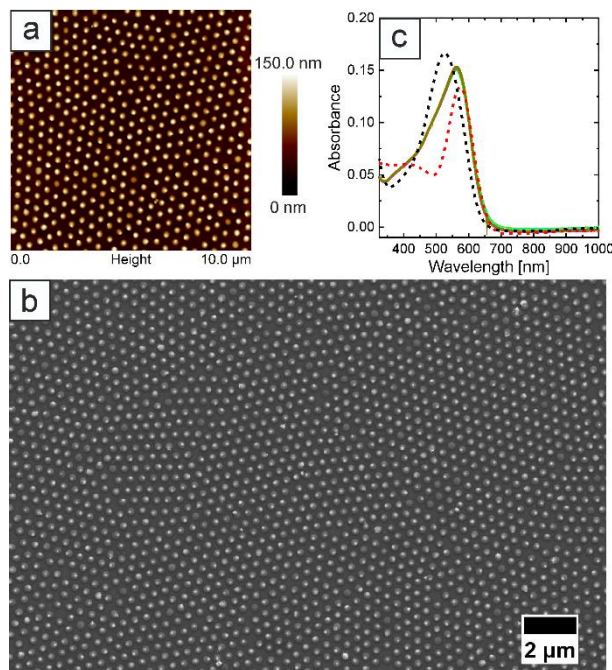


Figure 5. Mixed particle monolayer on glass prepared from a 1:1 mixture (by weight) of Ag40@Au20-PNIPAM and Au36@Au20-PNIPAM particles. (a) AFM height profile, (b) FE-SEM image of the mixed monolayer, (c) UV-Vis absorbance spectra measured at five different positions of the sample (solid lines). Note, that the spectra look almost identical. For comparison, the absorbance of Ag40@Au20-PNIPAM (black dashed line) and Au36@Au20-PNIPAM (red dashed line) monolayers are included.

Figure 5 c shows absorbance spectra of the mixed monolayer recorded at five different positions of the sample. The spectra match very nicely which manifests the random but homogeneous distribution of the Ag@Au-PNIPAM and Au@Au-PNIPAM particles throughout the whole monolayer.

Additionally, the absorbance spectra of monolayers prepared from the single systems, Ag40@Au20-PNIPAM (black dotted line) and Au36@Au20-PNIPAM (red dotted line), are included in the diagram for comparison. The peak wavelength and absorbance of the mixed monolayer are in between the properties of the individual colloidal building blocks. Thus, blending of Ag@Au-PNIPAM and Au@Au-PNIPAM particles is a quick and easy technique to further tune the absorption and scattering properties of the particle arrays.

Conclusions

With this work, we provide an experimental example of easily fabricated, macroscopic, plasmonic monolayers with controlled surface coverage, where the plasmonic properties are systematically varied through the chemical pre-treatment (core overgrowth) of one type of

colloidal core-shell building blocks. Seeded growth was applied as a versatile protocol to tune the dimensions, composition, and hence, the optical properties of the plasmonic cores with almost nanometre precision. Our synthetic protocol based on Au-PNIPAM core-shell colloids produces neither secondary nucleation nor non-spherical side products, allowing the synthesis of a library of monodisperse, spherical metal particles with core sizes ranging from 20 to 100 nm in diameter. Furthermore, self-assembly at the air/water interface was applied as a sophisticated technique that allows for surface patterning with highly ordered particle monolayers. This approach works for all the particles in our library. The obtained monolayers have uniform surface coverage and inter-particle distances. Due to the difference in core size and composition, we can adjust the LSPR position of the monolayers between 484 and 573 nm by the choice of the building blocks. We demonstrated that blending of core-shell particles with different cores is easily possible, providing another handle on optically fine tuning the plasmonic properties of colloidal coatings. In the future, reducing the hydrogel shell dimensions of the core-shell particles may allow for the realization of smaller inter-particle separations in the monolayer. In this case, plasmon resonance coupling might be usable as another parameter to tune the plasmonic properties of the monolayer.

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Supporting Information

Analysis of particle monolayers by SEM

Figures S1-S8 show SEM images of the Agy@Au20-PNIPAM and Aux@Au20-PNIPAM monolayers on glass substrates. The SEM images were taken of the same substrates, which were investigated by AFM as shown in figure 3.

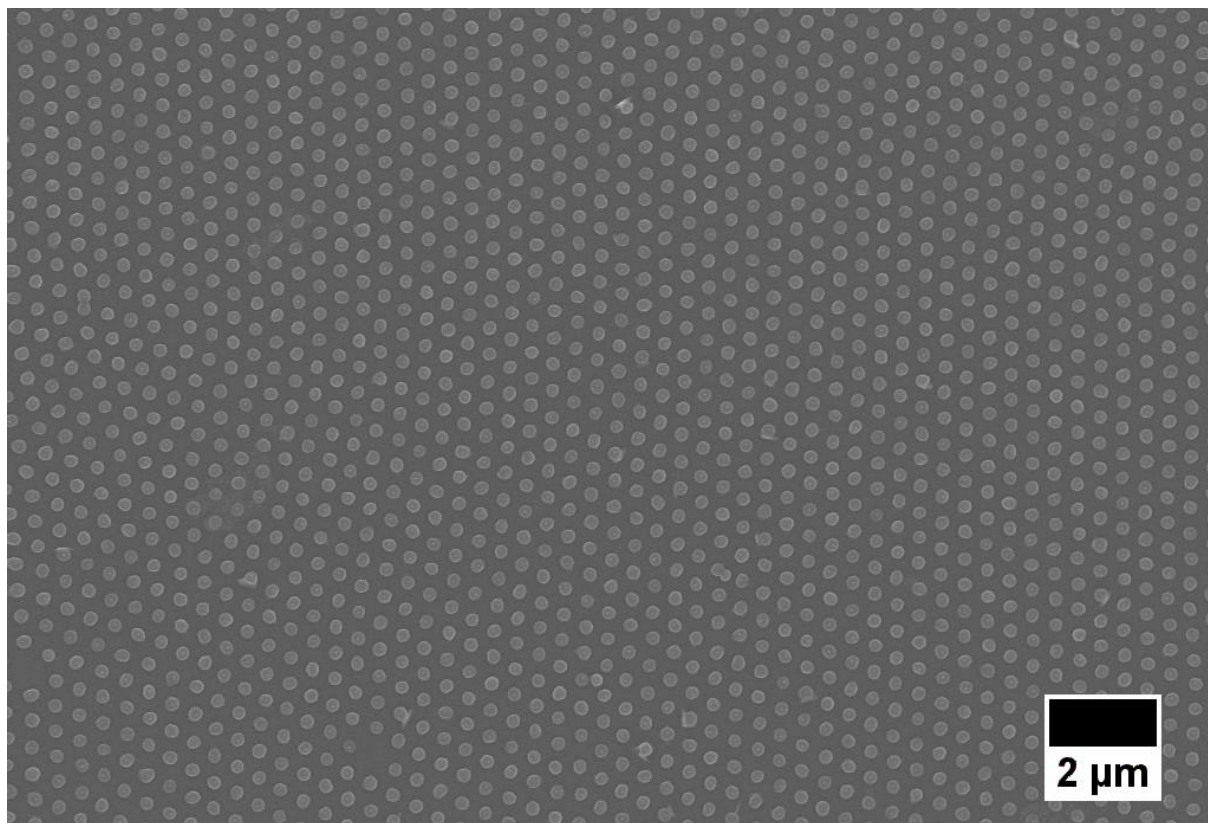


Figure S1. SEM image of the Au5@Au20-PNIPAM monolayer.

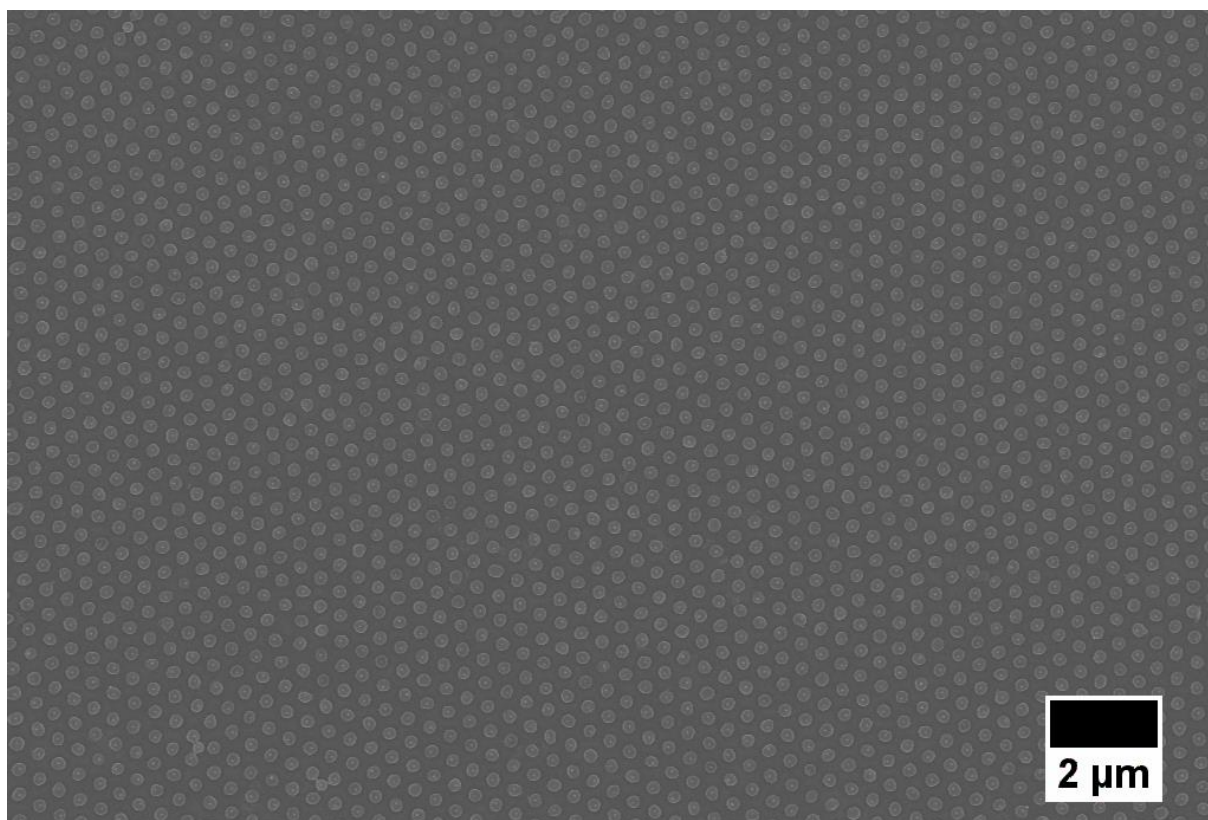


Figure S2. SEM image of the Au10@Au20-PNIPAM monolayer.

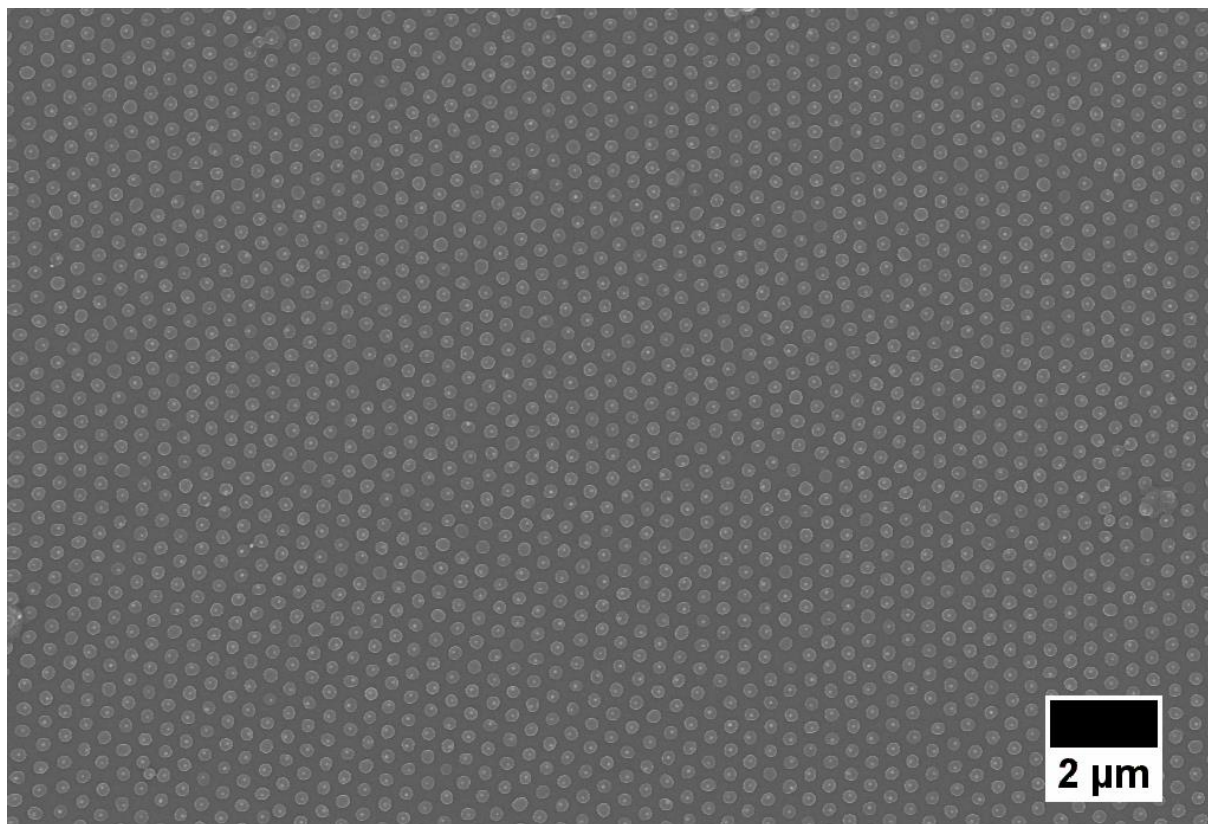


Figure S3. SEM image of the Au20@Au20-PNIPAM monolayer.

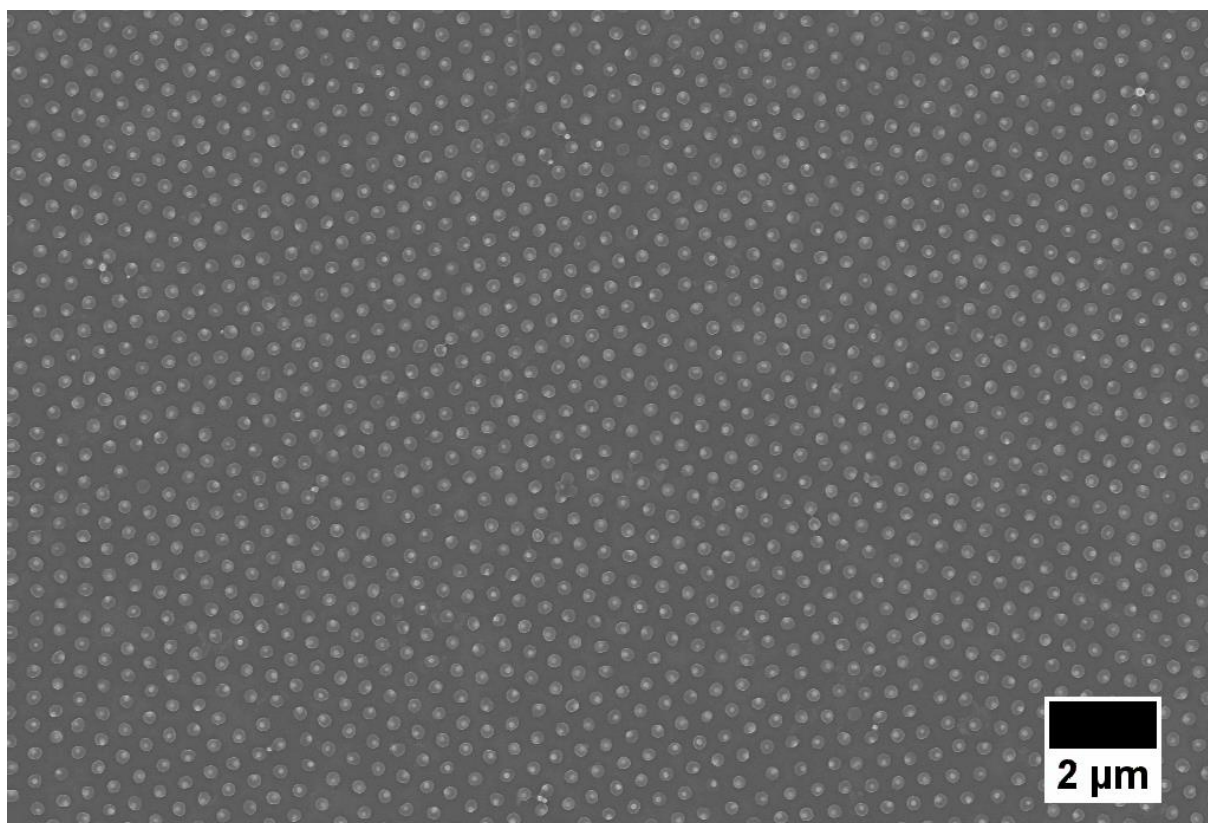


Figure S4. SEM image of the Au₃₆@Au₂₀-PNIPAM monolayer.

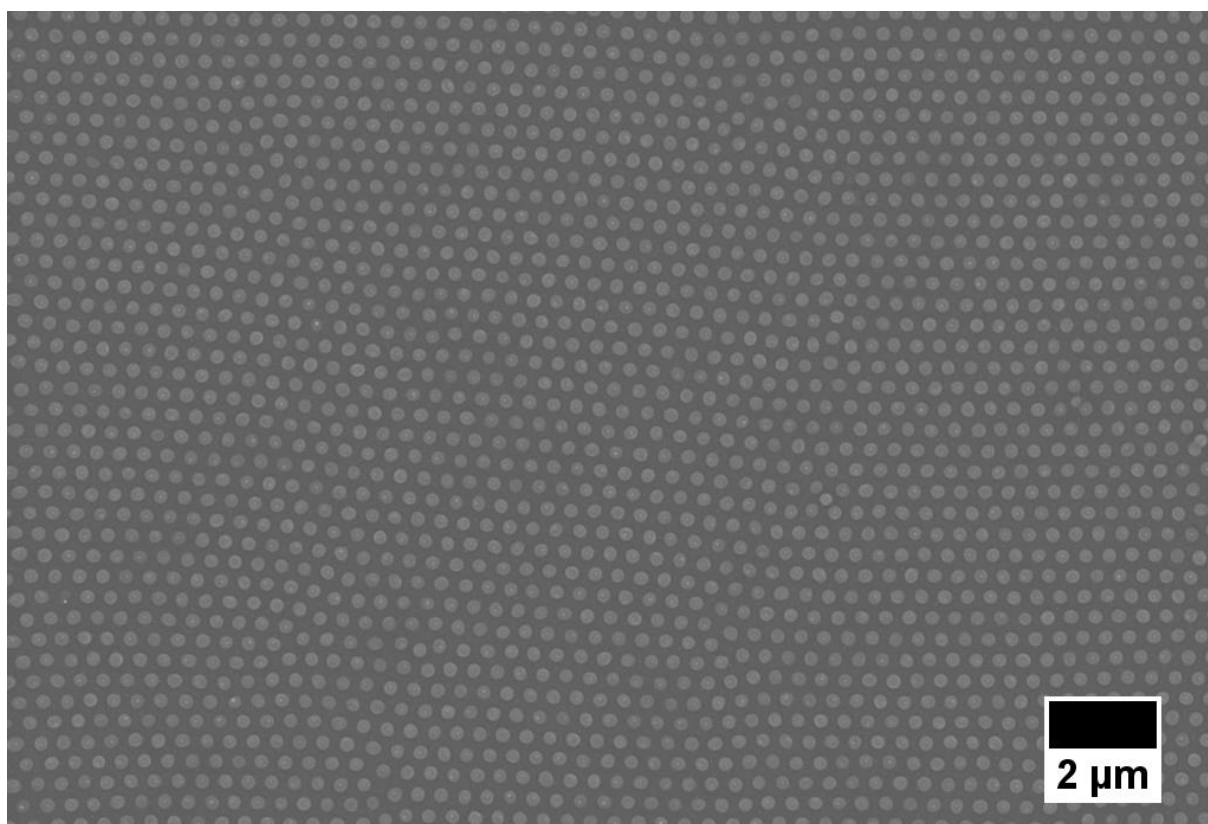


Figure S5. SEM image of the Ag₄@Au₂₀-PNIPAM monolayer.

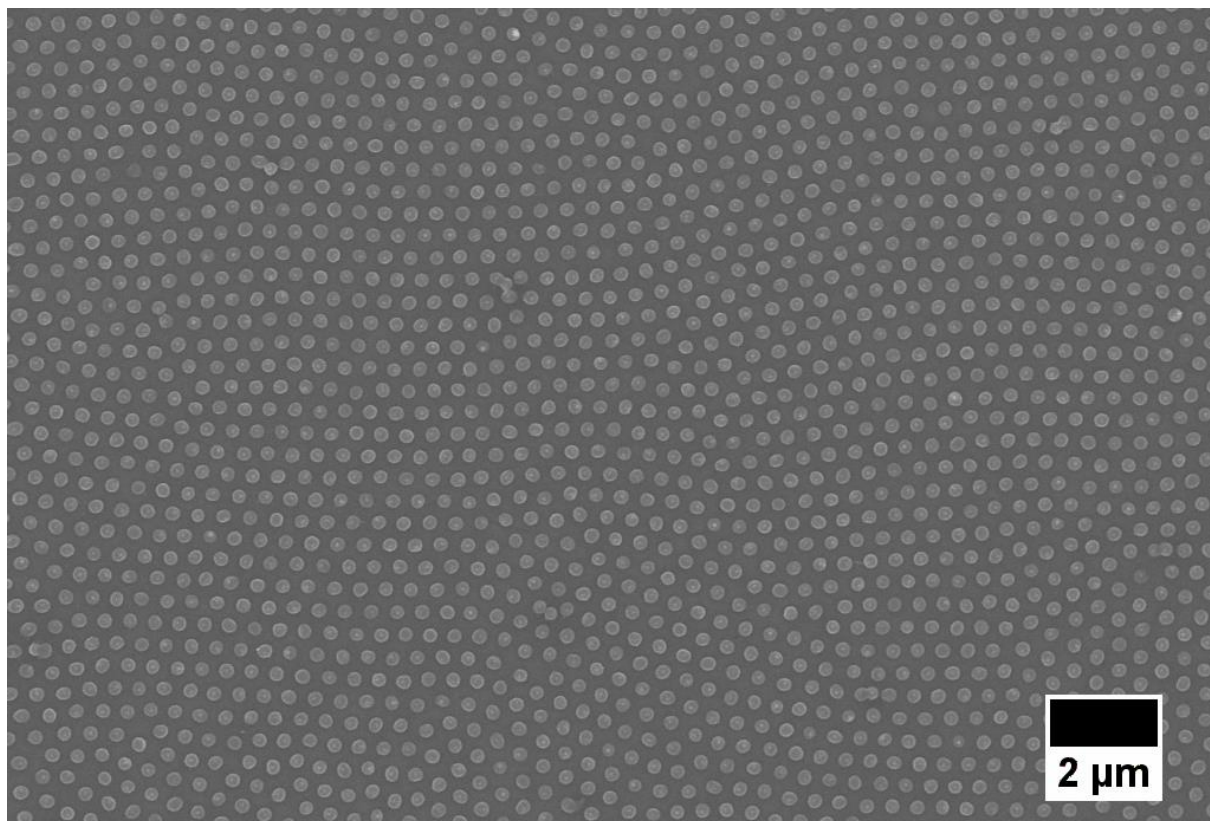


Figure S6. SEM image of the Ag13@Au20-PNIPAM monolayer.

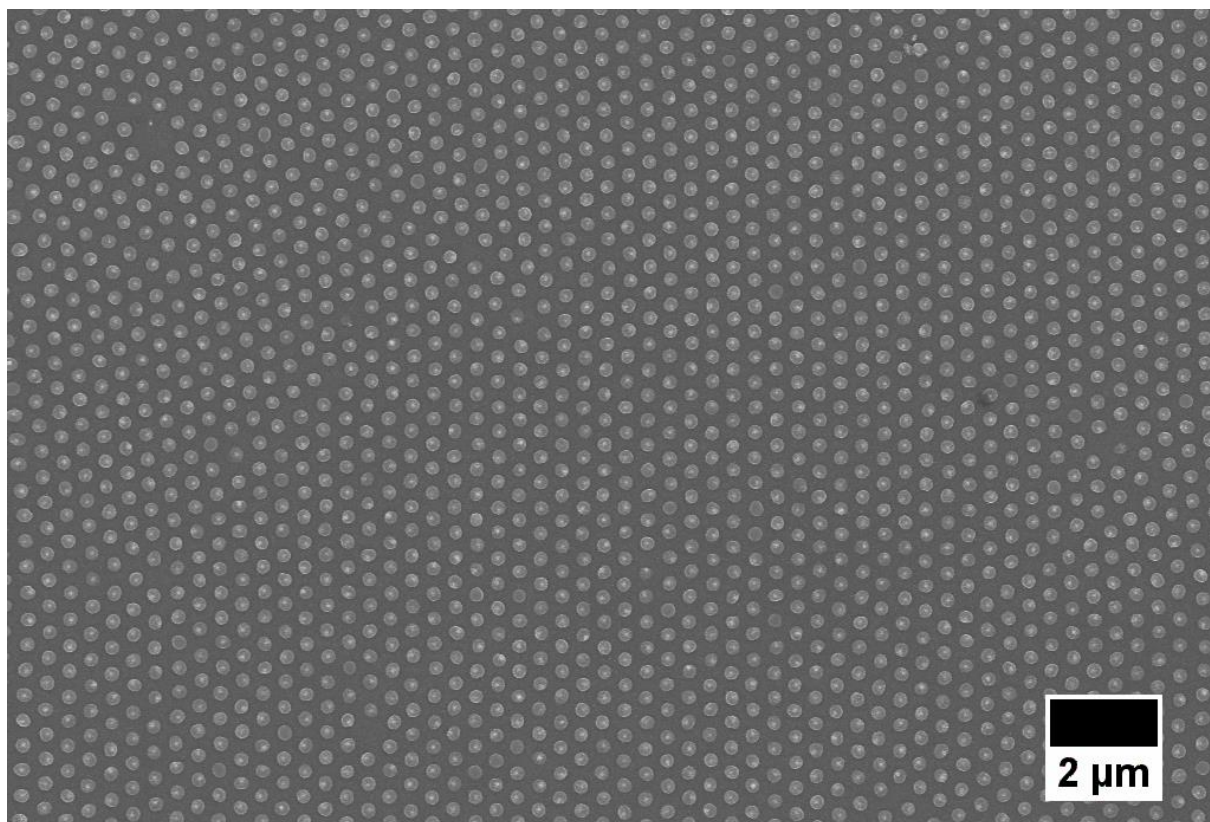


Figure S7. SEM image of the Ag26@Au20-PNIPAM monolayer.

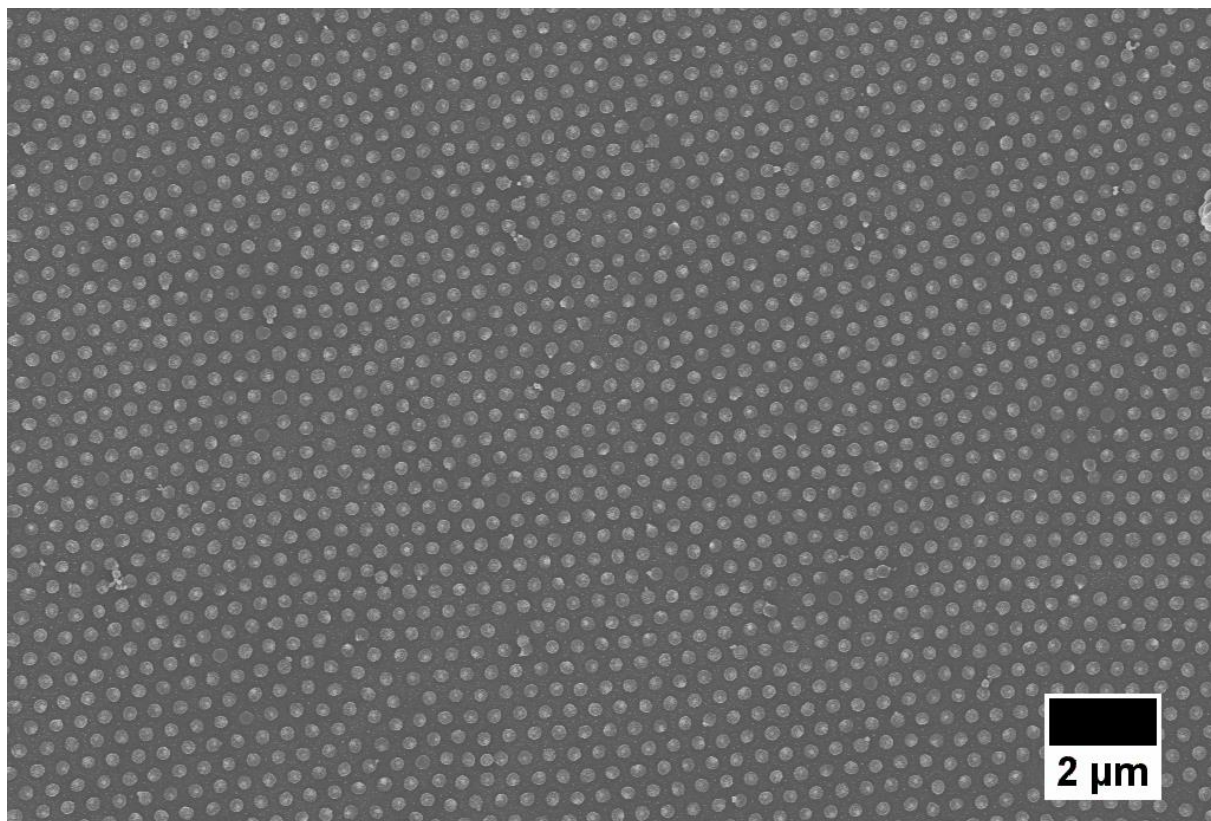


Figure S8. SEM image of the Ag40@Au20-PNIPAM monolayer.

4 Time-Controlled Colloidal Superstructures: Long-Range Plasmon Resonance Coupling in Particle Monolayers

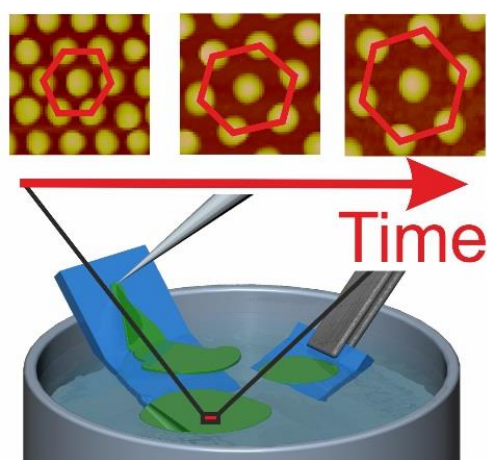
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Keywords: colloidal self-assembly, plasmon resonance coupling, core-shell particles, interface assembly, nanooptics



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Plasmon resonance coupling is a strongly distance dependent effect which has gained significant interest in the field of nano-optics. If realized in a controlled manner, this electromagnetic coupling opens pathways for the propagation of electromagnetic fields at the nanoscale, which is a prerequisite for all-optical computing and subdiffraction microscopy.¹ So far plasmonic coupling has been mostly exploited by investigating particle dimers or multimers utilizing linker chemistry such as DNA² or by creating plasmonic nanostructures via lithography³ or focused ion beam (FIB) milling.⁴ In all cases electromagnetic coupling is investigated on the single object level, i.e., measuring the interactions between two particles or clusters with rather small numbers of particles. A major challenge to advance the field of nanooptical technologies is the realization of structurally highly controlled plasmonic arrays in a parallel and scalable manner. Preferably, these are fabricated by readily available, wet chemically synthesized building blocks. Such colloidal arrays would result in macroscopic optical properties, which can be characterized by far-field spectroscopic techniques. Furthermore, precise structural control can allow access to collective optical effects. In this work we show pronounced collective optical features through the long-range plasmon resonance coupling in self-assembled colloidal monolayers with unusually large inter-particle distances (from 359 nm to 575 nm). Theoretical simulation using the coupled dipole approach⁵ supports the experimentally observed coupling leading to enhanced resonance peaks with narrow band width. The colloidal monolayers were fabricated by self-assembly of metal-hydrogel core-shell particles using interface-assisted self-assembly. Time has been used as a convenient parameter to control the inter-particle separation and hence the coupling strength.

Silver@gold-poly-*N*-isopropylacrylamide (Ag@Au-PNIPAM) colloids with soft and deformable hydrogel shells were prepared by first encapsulating gold nanoparticles of 20 nm in diameter (as determined by transmission electron microscopy, TEM) into cross-linked shells of PNIPAM according to a well-established protocol.⁶ In the next step the gold cores were overgrown with silver using a stepwise growth method adapted from a protocol reported by Contreras-Caceres *et al.*⁷ The full experimental details can be found in the Supporting Information (SI).

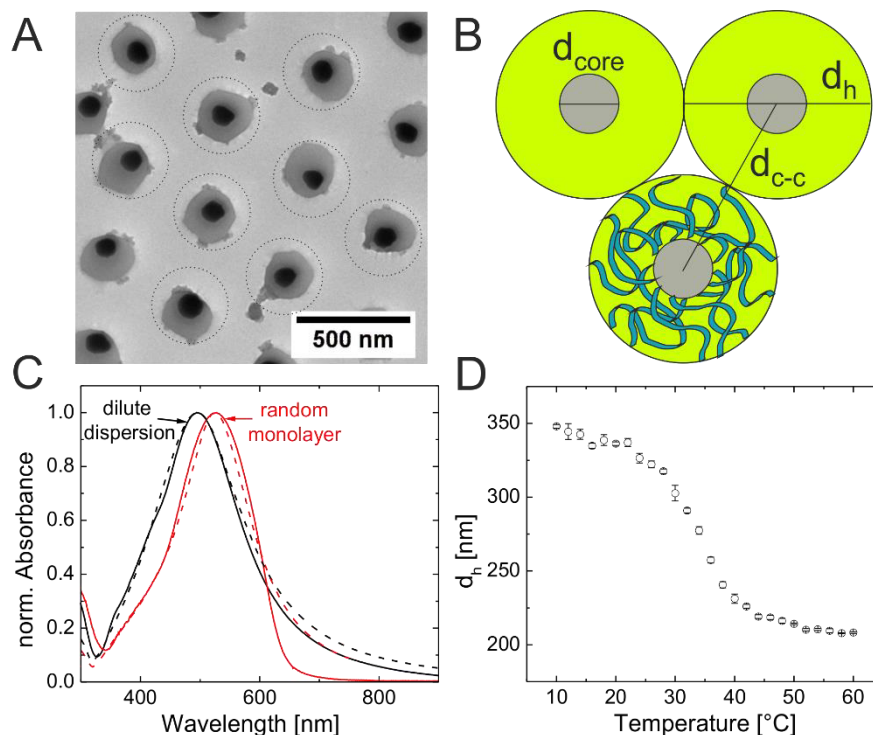


Figure 1. Characterization of Ag@Au-PNIPAM core-shell particles: A) Bright-field TEM image showing the particles in the dry state. The dotted circles indicate the hydrodynamic diameter measured by DLS in water at 20 °C. B) Schematic representation of 2D ordered superstructure in the wet state at an air/water interface with d_h , the hydrodynamic diameter, d_{core} , the core diameter and $d_{\text{c-c}}$, the nearest neighbor center-to-center distance. C) UV-vis absorbance spectra of particles in aqueous dispersion (black trace) and random monolayer on glass (red trace). The dashed lines are results from simulation using Mie theory (black trace) and the coupled dipole approach for a random monolayer (red trace). D) Evolution of the hydrodynamic diameter with temperature.

The spherical, plasmonic cores (Ag@Au) have an overall diameter d_{core} of 99.8 ± 6.3 nm as confirmed by TEM (Figure 1A). The TEM images also reveal the surrounding dried hydrogel shell as a gray corona. In contrast, in water the shell is swollen leading to an overall hydrodynamic particle diameter $d_h = 336$ nm at 20 °C (dotted line). Upon drying, significant shrinkage occurs and much smaller shell dimensions can be determined. This shell represents a low dielectric spacer between the plasmonic particles when the core-shell particles approach close proximity. Figure 1B shows a sketch of particles in the wet state with shell contact providing the characteristic length scales d_{core} , d_h and $d_{\text{c-c}}$ as the overall core diameter, the hydrodynamic core-shell diameter and the nearest neighbor center-to-center distance, respectively. Due to the nanoscale metallic core, these core-shell particles show a single localized surface plasmon resonance (LSPR) at 494 nm when measured in aqueous dispersion (black trace, Figure 1C). Mie theory⁸ establishes that this resonance is dominated by the dipole contribution, where the water swollen hydrogel shell has a refractive index of $n = 1.36$,⁶ just barely greater than water ($n = 1.33$). For a random monolayer of particles adsorbed on glass,

this resonance is slightly narrowed and shifted to 528 nm (red trace) due to the larger refractive index of the glass substrate ($n = 1.52$), the collapse of the hydrogel shell ($n = 1.45^9$), and weak interactions between particles. The primary interaction is a short-range coupling between single particle LSPR dipole resonances, as evidenced by the coupled dipole calculation⁵ for a random distribution of particles (dashed red trace). The details for the theoretical calculations can be found in the SI.

As a result of the lower critical solution temperature (LCST) of PNIPAM in water, the hydrogel shells undergo a temperature induced volume phase transition. Figure 1D shows the evolution of the hydrodynamic radius of the core-shell particles with temperature. At 20°C, where the PNIPAM shell is swollen, a hydrodynamic diameter d_h of 336 nm was determined. Upon increase in temperature the particles undergo pronounced shrinking with a transition temperature of approximately 34.5 °C. In the following hexagonally packed arrays of the core-shell particles were prepared by self-assembly at the air/water interface.¹⁰ Figure S1 in the Supporting Information (SI) schematically depicts the utilized assembly process. A crystallizing dish was filled with a dilute, aqueous solution of sodium dodecyl sulfate (0.05 mM) and a glass slide was placed inside the crystallizing dish at a tilt angle of approximately 45 °. Then a concentrated particle dispersion (0.5-1 wt% in MilliQ/EtOH: 50/50 by volume) was gently transferred onto the air/water interface via the glass slide using a syringe with a thin needle. This way a large (about 5 cm in radius), but freely floating monolayer of particles formed at the interface. The size of the floating monolayer can be easily tuned by the amount of floating dispersion applied. We would like to emphasize that assembly techniques such as spin- and dip-coating as well as vertical deposition are not suited for the preparation of comparable, cm-scale colloidal monolayers. Furthermore, in contrast to examples from the literature for interfacial adsorption of hydrogel particles in a Langmuir trough,¹¹ the presented monolayer does not cover the whole available surface area in our approach. Hence, the monolayer is not subjected to any barriers limiting the accessible surface area and is freely floating on the water surface. In order to transfer the monolayer from the interface to a solid substrate, hydrophilic glass substrates (1 cm²) were immersed below the monolayer and withdrawn at a shallow angle (Figure S1). The samples were dried using a heat gun blowing from the back side of the substrates. With this drying method the collapse of the hydrogel shell was only accelerated. The final morphology was found to be independent of the drying method. Due to the adhesion of the particles on the glass substrate we do not expect any positional changes after the monolayer is transferred to the substrate. This is manifested by the fact that the final particle diameter upon drying and the optical properties of the monolayer did not

change whether we dried the samples (slowly) in air or (fast) using a heat gun. Nevertheless the heat gun helped to reduce drying artefacts at the edges of the sample. This procedure was used to collect monolayers after different dwell-times, i.e., different durations after the particles were immobilized at the air/water interface. We found that the macroscopic shape of the floated monolayer islands did not significantly influence the final monolayer order and inter-particle distance as long as the island size was larger than the size of the glass substrate used for monolayer collection. Repetitions of the floating procedure and the monolayer transfer revealed very reproducible monolayer characteristics.

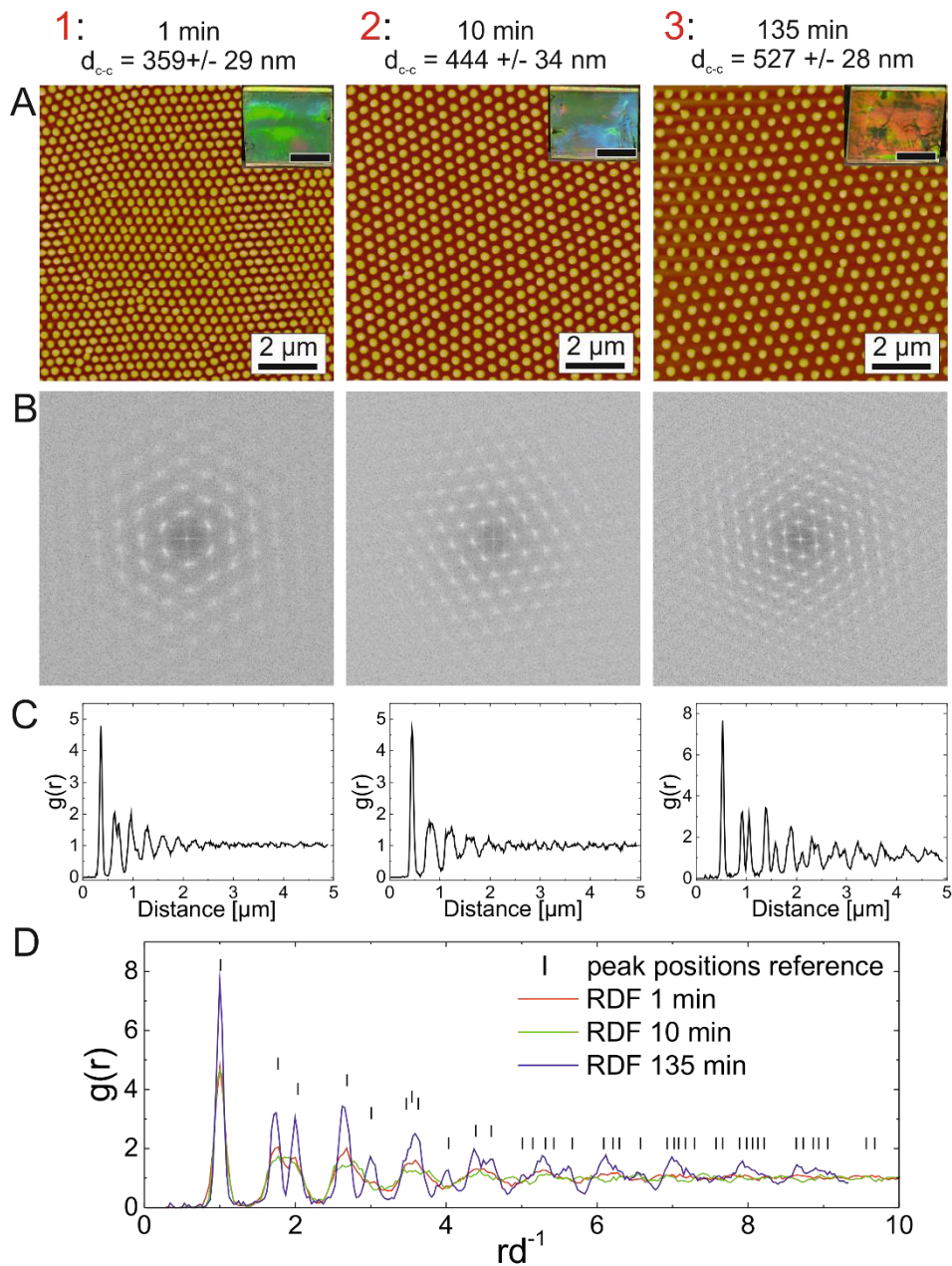


Figure 2. Structural characterization of a monolayer on glass withdrawn after 1 min (1), 10 min (2) and 135 min (3) dwell time: A) Atomic force microscopy (AFM) images (height profiles, each 10 x 10 μm²) recorded in tapping mode against air. The insets show digital photographs of the monolayers on glass slides of approximately 1 cm². The scale bars

correspond to 5 nm. B) Fast Fourier Transformations (FFT) of the AFM images and C) pair correlation functions $g(r)$. D) Pair correlation functions, $g(r)$ normalized to the nearest neighbor center-to-center distance of the monolayers (1-3) and a hexagonally close-packed reference monolayer (peak positions: black ticks).

Figure 2A shows AFM height profiles ($10 \times 10 \mu\text{m}^2$) of three monolayers of the same constituting particles, but withdrawn after different dwell-times (1 min (1), 10 min (2) and 135 min (3)). Each monolayer shows a highly regular, hexagonal packing of particles with large single-crystalline domains. The extraordinary high degree of order is emphasized by the Fast Fourier Transformations (FFTs) and pair correlation functions ($g(r)$) displayed in Figure 2B and C. The FFTs show strong Bragg peaks of many orders (4-7) characteristic for a long range hexagonal packing across many particle diameters. Apart from the similar degree of order of all monolayers, it can be clearly seen that the inter-particle distances d_{c-c} increase with the dwell-time. Nearest neighbor center-to-center distances d_{c-c} of 359 ± 29 nm, 444 ± 34 nm and 527 ± 28 nm, respectively, were obtained by measuring the first peak in each $g(r)$.^{11a} This means that the particle separation increases by almost a factor of 2 during 135 min of dwell-time starting with a d_{c-c} , which nicely agrees with the hydrodynamic equilibrium diameter in the swollen state in a MilliQ/EtOH mixture (50/50 by volume) of $d_h = 334 \pm 13$ nm.

The reason for this increase in inter-particle distances is the deformation of the hydrogel shell and potentially the particle position at the air/water interface. This extension of the monolayer is the result of a complex interplay between different forces such as interfacial tension, interface deformation, polymer elasticity and osmotic pressure imbalances due to hydrogel deformation. The exact balance and role of these forces is not yet fully understood and will be addressed in a future work. However, due to the high degree of order for all studied monolayers, independent on the degree of monolayer extension, attractive forces between the particles have to be present in all cases. Furthermore the strong deformation of soft hydrogels adsorbed at fluid/fluid interfaces has been observed previously.^{11a} The very slow dynamics of the monolayer extension hint to a cooperative effect. Results from the analysis of monolayers withdrawn after many more dwell-times can be found in the SI Figure S3A. The increasing d_{c-c} from sample 1 to sample 3 becomes also visible in the decreasing spatial frequencies of the diffraction pattern shown in the FFTs. Supporting the impression from the FFT images, the pair correlation functions show 7-10 peaks, with positions characteristic for hexagonally packed structures. The increasing degree of order also becomes visible when determining the hexagonal order parameter in dependence of d_{c-c} . For small inter-particle distances, i.e. short dwell times, a hexagonal order parameter of 0.6 was obtained. This value improved slightly with longer dwell times. At an inter-particle distance of 527 nm we could determine a maximum hexagonal bond

order parameter of 0.8. A summary of all determined bond order parameters is provided in Figure S2B in the SI. The high degree of order becomes even more evident when $g(r)$ is normalized to d_{c-c} and compared to $g(r)$ of a perfectly hexagonally packed reference monolayer (Figure 2D). Here the peak positions of the colloidal particle monolayers fit exactly the theoretically determined peak positions emphasizing the high degree of order.

In order to investigate the plasmonic properties of the self-assembled monolayers, we performed UV-vis extinction spectroscopy. For the three selected samples shown in Figure 2A, pronounced plasmon resonances, similar to the LSPR measured in solution, were measured (Figure 3A-C). For each sample, measurements were performed at 5 different positions with a spot size of 6 mm^2 . Here the strong plasmonic properties of the core-shell particles are exploited as an indicator for surface coverage and inhomogeneity in coverage. As can be clearly seen for each sample the spectra collected at different sample positions overlap nearly perfectly. This is a proof of the superior homogeneity of the monolayers over the entire size of the substrate. This optical homogeneity is an important prerequisite for the application of such structures as optically active coatings as well as their macroscopic characterization.

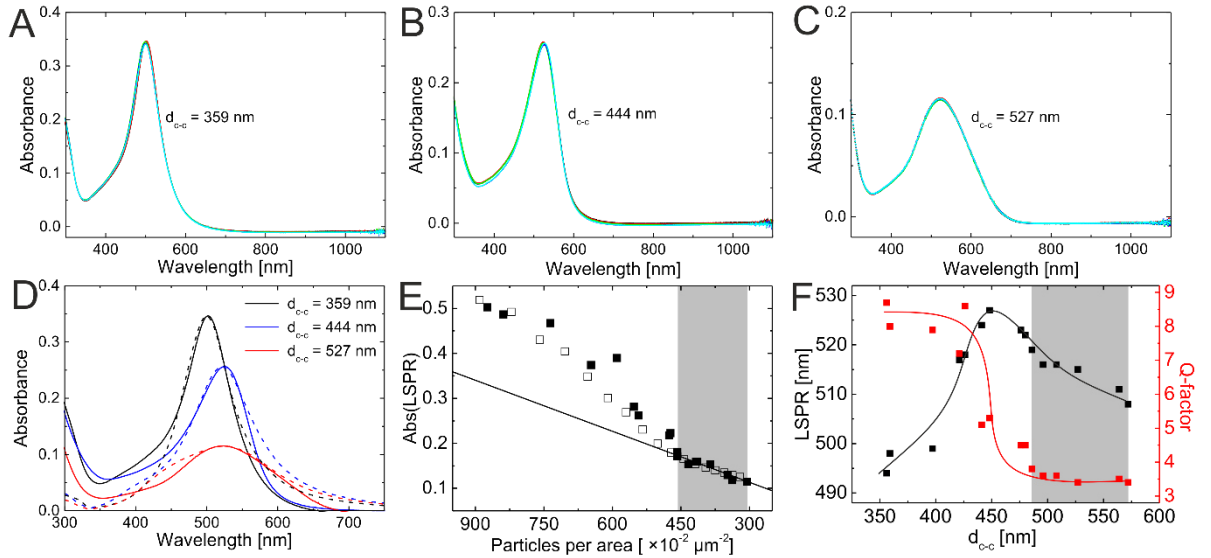


Figure 3. UV-vis spectra from different sample positions of the monolayer withdrawn after 1 min (A), 10 min (B) and 135 min (C) dwell time. Measurements with a spot size of 6 mm^2 performed at 5 different positions of the macroscopic substrate (1 cm^2) are plotted here. D) Comparison of experimental spectra obtained from single positions of the different monolayer (solid lines) with results from simulation using the coupled dipole approach (dashed lines). E) Maximum absorbance at the plasmon resonance peak as a function of the number of particles per area (filled symbols). The open symbols represent data points obtained from simulation using the coupled dipole approach. The solid black line is a linear fit of the data points through the origin in the regime of low particle densities. The gray shaded area indicates the non-coupling regime. F) Correlation between plasmon resonance position (black trace) and Q-factor (red trace) with d_{c-c} . The gray shaded area indicates the non-coupling regime. The solid lines are guides to the eye.

Having a closer look at the resonance peaks measured for the different monolayers, one observes a significant difference in the width, position and intensity of the resonance. The sample with the smallest inter-particle distance ($d_{c-c} = 359$ nm), corresponding to 840 particles/ $100 \mu\text{m}^2$, shows the narrowest plasmon resonance at 500 nm and a maximum absorbance of 0.35. The second sample ($d_{c-c} = 444$ nm, 540 particles/ $100 \mu\text{m}^2$) shows an absorbance of 0.26 and a LSPR position of 522 nm. The third sample ($d_{c-c} = 527$ nm, 388 particles/ $100 \mu\text{m}^2$) exhibits the broadest LSPR peak with a maximum at 524 nm and an absorbance of 0.12. Whereas the peak position and width of the sample with $d_{c-c} = 527$ nm is in good agreement with the result obtained for the random monolayer shown in Figure 1C, the monolayer with smaller values of d_{c-c} show a blue-shift of the resonance and a narrowing of the plasmon mode. The full width at half maximum (FWHM) values decrease from 159 nm for sample 3 to 62 nm for sample 1 leading to quality factors (Q-factor) of 3.24 and 8.03, respectively. The Q-factor is defined as the LSPR position divided by its FWHM. The strong decrease in FWHM indicates pronounced dipolar coupling in the particle monolayer with d_{c-c} of 359 nm. This narrowing of the mode leads to a much higher Q-factor and hence an enhancement of the strength of the plasmon mode.

To support the experimental findings, we performed theoretical modeling of the optical properties using the coupled dipole approach.^{5, 12} In order to describe the observed broadening of the plasmon resonance with increasing inter-particle distance, we introduced an attenuation factor with a characteristic exponential decay length ℓ_{atten} . This attenuation restricts the range of weak dipolar coupling to a certain length scale, much larger than ℓ_{atten} , and sufficiently damps strong dipolar coupling for larger inter-particle distances. A good theoretical description of the experimental data could only be achieved by using such a restriction of the coupling range. All monolayer spectra shown in Figure 3A-C could be described by using an average $\ell_{\text{atten}} = 210 \pm 110$ nm independent of the inter-particle-distance. Figure 3D compares the experimental spectra for the three monolayers with the results from theoretical fitting. The resonance positions as well as the width of the resonance modes match very well between experiment and fit. The physical justification for introducing ℓ_{atten} as an additional fit parameter is as follows: 1) Our hexagonal monolayer are not perfectly ordered. The position of the metal cores deviates to a certain extent from perfect hexagonal packing. In addition the monolayer contain crystalline domains of different orientations and grain boundaries. These effects weaken the mean coupling strength. 2) The refractive index environment is not isotropic and rather complex due different contributions from the collapsed hydrogel shell, the glass substrate and the surrounding medium (air, $n = 1.00$).⁹ Hence the environment represents a lossy medium reducing long-range,

coherent dipole-dipole interactions. A complete description of the simulation layout and the fitting procedure can be found in the SI.

To further investigate the plasmonic coupling and its dependence on d_{c-c} and surface coverage, results for fifteen monolayers withdrawn after different dwell-times are summarized in Figure 3E and F. According to Lambert-Beer law we expect a direct correlation between the absorbance and the concentration (here particles per unit area, i.e., particle density) following a linear relation. Hence the absorbance at the LSPR maximum was chosen as a first measure to analyze the optical properties of our monolayer. Figure 3E depicts the dependence of the absorbance at the LSPR position on particle density. Indeed a linear dependence is found for low particle densities between 440 and 300 particles/100 μm^2 as indicated by the linear fit through the origin (solid line). It is clearly visible that the last data points, at low particle density, are nicely described by the linear fit. This region is highlighted by the gray shaded area in Figure 3E. In contrast, for higher particle density a significant deviation from the linear dependence is observed, and the absorbance increases more than expected from Lambert-Beer law. In particular for particle densities > 600 particles/100 μm^2 a strong mismatch between the experimentally determined absorbance and the linear expectation is found. This indicates resonance coupling between the silver nanoparticle cores at high particle densities, i.e., small inter-particle distances. This experimental behavior can be well supported using results from the attenuated coupled dipole approach. Theoretical simulation for various inter-particle distances covering the relevant experimental range gives similar results as the experiment. This confirms that dipole-dipole interactions in our monolayer are indeed distance dependent leading to stronger absorbance in the coupling regime, i.e., at medium and high particle densities.

Since plasmon coupling appears to be a strongly distance dependent feature, we analyzed the evolution of the LSPR position (black trace) and the quality factor (Q-factor) with d_{c-c} as shown in Figure 3F. For small inter-particle distances (356-448 nm) a steep increase in LSPR wavelength (494 nm to 527 nm) for increasing d_{c-c} is found. In this region the Q-factors are between 8 and 9. These values are much higher than the Q-factor of 3.1 determined from a spectrum of an aqueous particle dispersion (see Figure 1C). The 2-3 times higher Q-factors for small inter-particle distances < 430 nm are related to plasmon resonance coupling. To the best of our knowledge such strong plasmon coupling has not been previously reported for macroscopic arrays of self-assembled plasmonic colloids with inter-particle distances in the hundred nm range. For larger inter-particle distances the LSPR position starts to blue shift in an almost linear fashion reaching a final value of 508 nm for the sample with $d_{c-c} = 575$ nm. Simultaneously the Q-factor drops to almost constant values between 4 and 3 in the gray shaded

area, which marks the non-coupling regime. The nearly constant values of the Q-factor, close to the value obtained for an aqueous particle dispersion (3.1), underline that coupling is not present for the largest inter-particle distances studied.

In summary we have demonstrated a versatile method to prepare colloidal monolayers, which exhibit extraordinarily high degrees of order and inter-particle distances that are easily tunable with time. We made use of the unique, soft and deformable character of hydrogels to tailor the periodicity of plasmonic particle arrays. The accessible inter-particle distances range from 350 nm to 575 nm by simply varying the dwell-time for monolayer extraction from the air/water interface. Using one single type of Ag@Au-PNIPAM nanoparticles, we demonstrated that the macroscopic properties of this plasmonic superstructure can be widely varied from coupling to non-coupling. This is reflected in a shift of the LSPR resonance over 30 nm, an extraordinarily high absorbance and an increased Q-factor. The Q-factor is about 3 times higher in the coupling regime as compared to non-coupling samples. This work is a crucial step towards ‘colloidal nanooptics’ and opens new pathways to applications of plasmonic colloids in nanooptical devices. The attenuated coupled dipole approach used to describe our experimental findings underlines the importance of the refractive index environment on long-range dipolar coupling and allows prediction of future design rules for the fabrication of self-assembled plasmonic monolayer with much higher coupling strength.

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Supporting Information

Experimental details

Materials. Gold (III) chloride trihydrate (Sigma-Aldrich, $\geq 99.9\%$), sodium citrate dihydrate (Aldrich, $\geq 99\%$), sodium dodecylsulfate (SDS; Merck), butenylamine hydrochloride (BA; Sigma-Aldrich, 97%), *N*-Isopropylacrylamide (NIPAM; Sigma-Aldrich 97%), *N,N'*-methylenebisacrylamide (BIS; Fluka, $\geq 98\%$) potassium peroxodisulfate (PPS; Fluka, $\geq 99\%$), L-ascorbic acid (reagent grade, Sigma Aldrich), ammonium hydroxide solution (30-33 %, Sigma-Aldrich), ethanol abs. (99.1-100 %, VWR Chemicals), glycine ($\geq 99.7\%$, Merck), hexadecyltrimethylammonium bromide ($\geq 96.0\%$, Fluka), silver nitrate (puriss. p.a. $\geq 99.5\%$, Fluka) and sodium hydroxide (1 M, Grüssing) were used as received. Purified water from a Milli-Q system (Millipore) with a final resistivity of 18.2 M Ω cm was used for all synthesis, purification and assembly steps. All glassware was cleaned using aqua regia and thoroughly rinsed with water, acetone and ethanol.

Synthesis and Functionalization of Gold Nanoparticles. Gold nanoparticles of ~ 20 nm in diameter as determined from TEM were prepared by the well-known method of Turkevich using citrate as reducing agent.¹ Briefly, 200 mL of 5×10^{-4} M HAuCl₄ was heated until heavy boiling while being continuously stirred. Then 10 mL of a preheated aqueous solution of trisodium citrate (0.67 wt%) were added quickly and boiling was continued for 20 min. Afterwards the deeply red gold nanoparticle dispersion was allowed to cool to room temperature.

1.2 mL of a 0.624 mM aqueous SDS solution was added to 200 mL of the previously prepared gold particle dispersion at room temperature. After 20 min of stirring following the SDS addition, 0.392 mL of a 2.88 mM butenylamine hydrochloride solution in ethanol was added dropwise and stirring was continued for 20 min. Finally, the gold nanoparticles were concentrated by four centrifugation steps for 90 min at 3300 rcf. The residues were collected and stored in the dark at room temperature.

Hybrid Microgel Preparation. The functionalized gold nanoparticles were encapsulated into hydrogel shells by seeded precipitation polymerization.² A total of 100 mL of water containing 0.02 M NIPAM and 15 mol% of BIS (referred to the monomer) were mixed in a three-neck round bottom flask (250mL) and heated to 70 °C using an oil bath and a magnetic stirrer. Additionally, the flask was equipped with a reflux condenser and the reaction solution was

¹ J. Turkevich, P.C. Stevenson, J. Hillier, *Discussions of the Faraday Society* **1951**, 11, 55.

² M. Karg, S. Jaber, T. Hellweg, P. Mulvaney, P. *Langmuir* **2011**, 27, 820.

degassed with nitrogen for 30 min. Afterwards, 2.35 mL of the functionalized gold particles in water ($[Au] = 0.01 \text{ M}$) was added dropwise and after 15 min of equilibration time the polymerization was started by the rapid addition of 2 mg of potassium peroxodisulfate dissolved in 1 mL of water. The red and almost clear particle dispersion became slightly turbid within the first 15 min of reaction time. Two hours after the addition of the initiator, the dispersion was allowed to cool down to room temperature. Cleaning of the Au-PNIPAM core-shell hybrid particles was carried out by repeated centrifugation (90 min at 6500 rcf) and redispersion in water. Three steps of centrifugation and redispersion were performed. Finally, the particles were concentrated to an aqueous dispersion of 2 wt%.

Overgrowth of Au Cores. 6.00 g of glycine (80 mmol) and 3.64 g of CTAB (10 mmol) were dissolved in 200 mL of MQ water at 35 °C. After the solution was cooled to RT, 1 mL of an Au-PNIPAM dispersion (2 wt%) was added. Next 16 mL of a 0.1 M NaOH solution were added, followed by the addition of 9 mL of an ascorbic acid solution (100 mM). Then 13.1 mL of a freshly prepared $AgNO_3$ solution (15 mM), which was kept in the dark, were added stepwise to the reaction mixture. Every two minutes 655 μL of the solution were added quickly. After 20 addition steps stirring was continued for another 20 minutes before the reaction mixture was purified using centrifugation. The reaction mixture was diluted with MQ water (50 mL total volume) and centrifuged (1 h at 3740 rcf). This process was repeated two times using MQ water, two times with ethanol and again two times with MQ water for redispersion of the residues. After the last cleaning step the residue was redispersed in approximately 2 mL of MQ water.

Instrumentation

Transmission Electron Microscopy (TEM). A Zeiss CEM902 transmission electron microscope was used to characterize the core-shell particles in terms of size and morphology. The sample was prepared on carbon coated copper grids from solution and left to dry against air. Thereof the size and polydispersity of the core-shell particles was determined with the software ImageJ.

UV-Vis Extinction Spectroscopy. Absorbance spectra of the particles in solution were recorded with an Agilent 8453 UV-Vis Spectrometer in quartz cells with 1 cm light path. Measurements were performed at ambient conditions.

UV-Vis transmission spectra of the particle monolayers were recorded with a Cary 5000 2.23 in p- and s- polarization of the incident light with a detection angle of $\theta = 180^\circ$. The spectra

were recorded from 300 nm to 1100 nm. All spectra were background and substrate corrected and converted into absorbance spectra.

Atomic Force Microscopy (AFM). $10 \times 10 \mu\text{m}^2$ topographic AFM images were recorded with a Nanoscope Multimode AFM (Veeco) in tapping mode against air. OTESPA-R3 AFM probes (Bruker) were employed for image recording. The cantilevers possess a resonant frequency of approximately 300 kHz and a spring constant of approximately 26 N/m. The tip geometry was a visible apex with a nominal tip radius of 7 nm.

Self-Assembly at the Air/Water Interface³

Figure S1 shows the setup and procedure applied for colloid assembly at the air/water interface (1.) and the subsequent transfer onto solid supports (2.) in a schematic fashion. We filled a crystallizing dish with an aqueous solution of sodium dodecyl sulfate (0.05 mM) and placed a glass slide at a tilt angle of approximately 45° at the border of the dish. The concentration of the surfactant was optimized to yield highly ordered monolayer which show significant changes in inter-particle distances as a function of dwell time. This concentration however cannot be generalized to other colloidal systems and hence may yield to monolayers of lower quality for other colloidal materials. Our core-shell colloids were immersed at the air/water interface by gentle transfer of a concentrated particle dispersion (0.5-1 wt% in MilliQ/EtOH: 50/50 by volume) via the glass slide using a syringe with a thin needle. The freely floating monolayer at the interface was transferred onto hydrophilic glass substrates (1 cm^2) by immersing the substrate below the monolayer and withdrawal at a shallow angle.

³ N. Vogel, S. Goerres, K. Landfester, C. K. Weiss, *Macromol. Chem. Phys.* **2011**, 212, 1719.

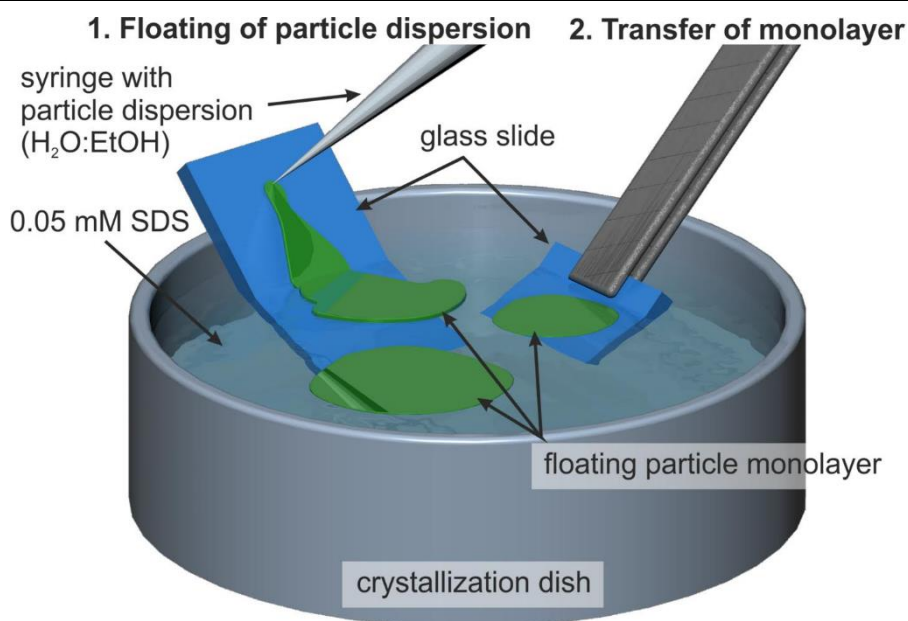


Figure S1. Schematic representation of the colloidal self-assembly process at the water/air interface and the withdrawal and transfer of the monolayer onto solid supports.

Monolayer Homogeneity

Figure S2 provides AFM height profiles measured at different positions of a particle monolayer close to the edge of the monolayer. The monolayer under investigation was collected from the air/water interface in a way that the substrate was only partially below the monolayer during withdrawal. This way only parts of the substrate were coated with the particle monolayer and the edge of the monolayer became accessible for analysis. The AFM images clearly show a rather unordered monolayer with larger inter-particle distances at the very edge of the monolayer. Already at approximately 80 μm away from the edge, the monolayer is highly ordered with hexagonal particle arrangement and inter-particle distances which remain nearly constant when going further towards the center of the monolayer.

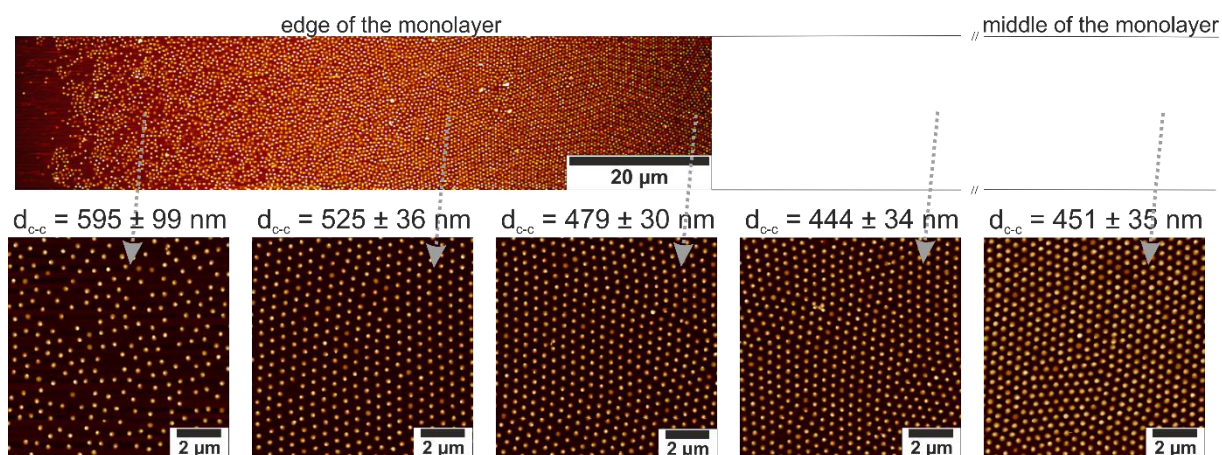


Figure S2. Characterization of the particle monolayer by AFM: Evolution of d_{c-c} from the edges of the particle monolayer towards the middle.

Dwell-Time Dependence of the Interparticle Distance

Figure S3A shows the center-to-center distance as a function of dwell-time. d_{c-c} was calculated by determining $g(r)$ from analysis of $10 \times 10 \mu\text{m}^2$ AFM images from monolayer transferred onto glass substrates after different dwell-times. For the image analysis the particles at the edges of the images were excluded. At the beginning of the floating process the increasing d_{c-c} evolves rather fast within the first ten minutes and then slows down but steadily continues for up to three hours. Upon the first contact of the particle dispersion with the air/water interface a d_{c-c} of 359 nm is found. This value is close to the hydrodynamic particle diameter in dispersion of 334 nm. After a dwell-time of approximately 150 minutes a final d_{c-c} of 575 nm is observed. This increasing inter-particle distance is accompanied by an improvement of the hexagonal bond order parameter as depicted in Figure S3B. Samples withdrawn after 1 minute of dwell time possess a hexagonal bond order parameter of 0.60. This parameter improves with longer dwell times, i.e. larger inter-particle spacing, to 0.80. A perfect hexagonal reference pattern, indicated by the blue line, possesses a hexagonal bond order parameter of 0.94. This comparison reveals the high quality of our prepared monolayers independent of the dwell time.

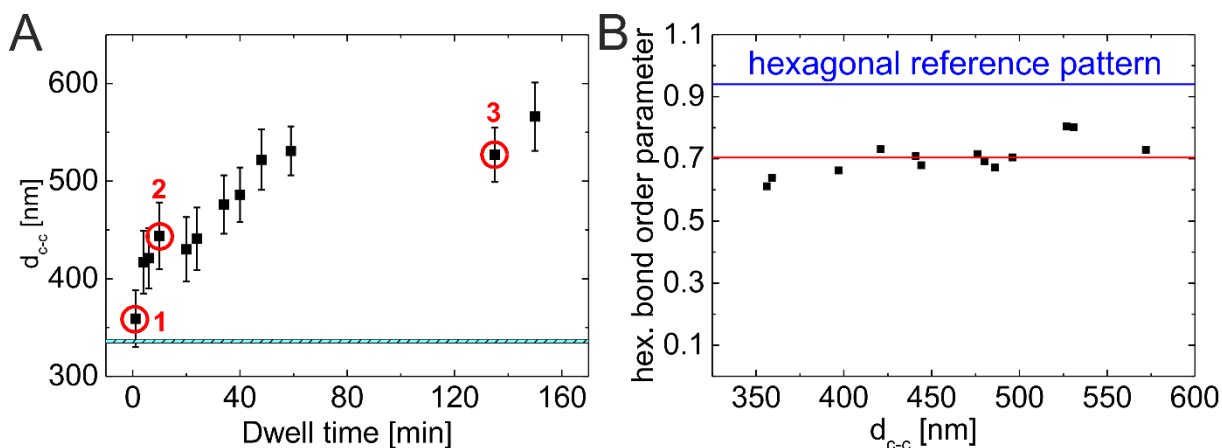


Figure S3. A) Development of d_{c-c} with dwell time at the air/water interface. The red circles highlight samples which were thoroughly discussed in the main manuscript. The shaded area marks the range of hydrodynamic diameter d_h obtained from DLS in the various floating dispersions (MilliQ/EtOH mixtures, pure MilliQ, pure EtOH). B) Calculated bond order parameters as a function of d_{c-c} . The blue line indicates the hexagonal bond order parameter of a reference pattern and the red line shows the average hexagonal bond order parameter of the monolayers.

Theoretical Calculations

Particles in Dispersion. The spectral response of the core-shell particles dispersed in water was calculated via Mie theory using Mathematica 10, following the multilayer recursive method.⁴ A particle diameter of 100 nm, in agreement with experimental values from TEM, as

⁴ A. Moroz, *Annals of Physics* **2005**, 315, 352.

well as the optical constants for silver from Johnson and Christy⁵ were used. The external medium was water using the refractive index from Hale.⁶ As a first approach, the hydrogel shell was neglected, with the results shown in Figure S4A. The dipole alone and multipoles up to the fourth term were calculated, with a peak dipole resonance at 481 nm. The bare dipole mode (black) provides a better match to the experiment (gray), which shows no evidence of a quadrupolar mode. A better fit was found when the hydrogel shell was considered, as shown in Figure S4B, with the same dipole mode peak as the experiment at 495 nm. In this latter case, the hydrogel shell had a diameter of 330 nm, according to results from DLS measurements, and a best fit refractive index of $n_{\text{gel}} = n_{\text{H}_2\text{O}} + dn$, where $dn = 0.031$ ($n_{\text{gel}} = 1.366$ at a wavelength of 500 nm). This refractive index lies within the expected range for a swollen hydrogel with a water content of approximately 80 vol-%.⁷

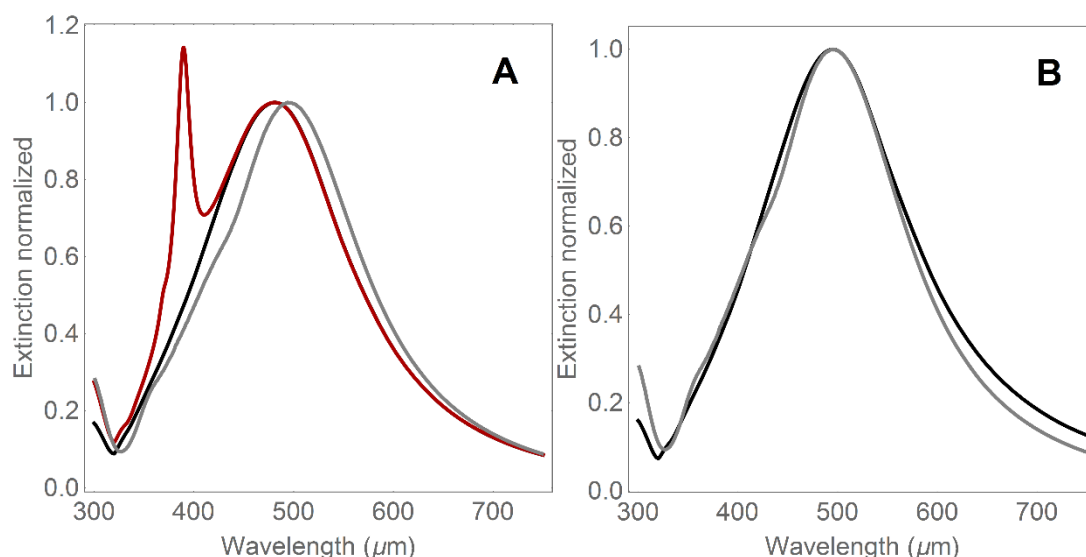


Figure S4. Mie theory calculated extinction spectrum of Ag nanoparticles in aqueous dispersion. The complete (red) and dipole only (black) contributions are compared to the normalized experimental absorbance data (gray). A) Without a hydrogel shell (water medium only), and B) with a hydrogel shell.

Random Monolayer on Glass. Mie theory is perfectly suited for particles of spherical symmetry in an effective medium (dispersion), but less ideal for particles adsorbed on a substrate such as glass, where the symmetry is broken. Thus we used a finite-element method (FEM) that can handle arbitrary shapes.

We used Lumerical finite-difference time-domain (FDTD) with a glass substrate and single Ag particle (100 nm in diameter) immersed in a constant background medium. The best fit FDTD result, with a background index of 1.43, is shown in black in Figure S5. While the peak dipole

⁵ P.B. Johnson, R.W. Christy, *Phys. Rev. B* **1972**, 6, 4370.

⁶ G.M. Hale, M.R. Querry, *Applied Optics* **1973**, 12, 555.

⁷ M. Karg, S. Jaber, T. Hellweg, P. Mulvaney, *Langmuir* **2011**, 27, 820.

resonance occurs at nearly the same wavelength as the experimental spectrum, the shape is significantly broader, even without the quadrupole resonance (peak at 403 nm).

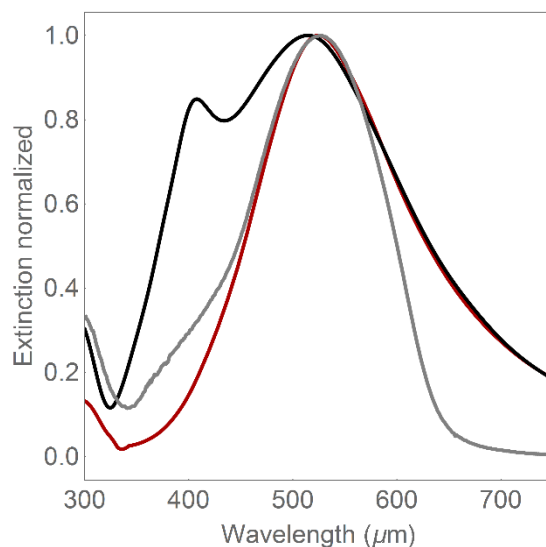


Figure S5. First attempts at simulating a random monolayer of Ag particles on glass. FDTD simulation (black) of a single Ag nanoparticle on glass and Mie theory simulation of a single nanoparticle in a background index of 1.334 compared to experiment (gray).

Subsequently we tried dipole mode Mie theory, fitting the experimental spectrum for the shell diameter and external medium index using a shell index of $n_{\text{gel}} = n_{\text{H}_2\text{O}} + 0.12 \approx 1.45$. The best fit results, shown in red in Figure S4, are with a shell diameter of 220 nm and a medium refractive index $n = 1.14$. Despite the geometry differences, the Mie dipole spectrum nearly exactly reproduces the broad dipolar resonance of the FDTD simulation result, especially at longer wavelengths. This is because the low refractive index contrast between the collapsed hydrogel shell and the glass substrate leads to reduced scattering and reflection at the substrate surface, significantly reducing the role of the substrate. However, the mismatch between both theoretical approaches and the experimental data indicates the inadequacy of a single-particle description. We will address this discrepancy after first investigating particle interactions in the context of highly ordered monolayers.

Hexagonally Ordered Monolayers on Glass. Plasmonic particles more than a diameter apart interact primarily through dipole-dipole coupling. Zou and Schatz described a method for calculating the induced polarization in a particle in response to incident light and interactions with surrounding particles.⁸ They formulated this response in terms of a dipole interaction matrix and linear polarizability equations, which can be solved through simple matrix reduction methods (here we used built-in Mathematica functions). This method allows rapid calculation

⁸ S. Zou, G.C. Schatz, *Nanotechnology* **2006**, 17, 2813.

of the lattice extinction coefficient. The coupled dipole method has recently been shown to agree with both experiment and more complete FDTD methods for lithographically-produced rectangular arrays, at significantly reduced computation times compared to FDTD.⁹

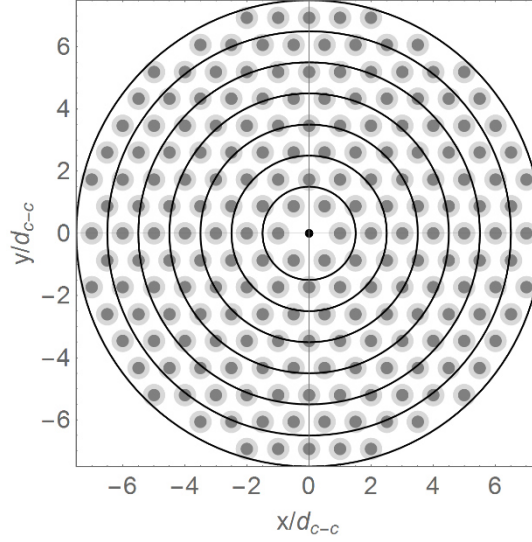


Figure S6. Hexagonal lattice organized into concentric shells. Lattice sites are represented by dark gray cores with light gray shells, though only the center location is important for the calculation.

The monodisperse Ag particles considered here can be modelled with identical polarization vectors, greatly reducing the set of simultaneous equations from $3N$ to 3. For our ordered monolayers, we consider the polarization response of a single particle at the center of a circular domain surrounded by a hexagonal lattice, as shown in Figure S6. The radius of the domain was extended until convergence of the dipole interaction matrix was achieved, typically 5-50 unit vectors.

The single particle polarization was calculated from Mie theory with the same parameters as described for the random monolayer. As in that case, we performed a parameter sweep of the effective medium refractive index n_{med} , only in this case that index appears in both the Mie dipole polarizability term and in the coupled dipole interaction matrix. The external medium was modelled as an effective medium with values between 1.00 (for only air as medium) and 1.45 (for only collapsed hydrogel as medium) in increments of 0.025. To reduce computation time, we restrict our attention to the three examples shown in Figure 3 of the main text, namely lattices with $d_{c-c} = 359, 444,$ and 527 nm.

⁹ A.I. Väkeväinen, R.J. Moerland, H.T. Rekola, A.P. Eskelinen, J.P. Martikainen, D.H. Kim, P. Törmä, *Nano Lett.* **2014**, 14, 1721.

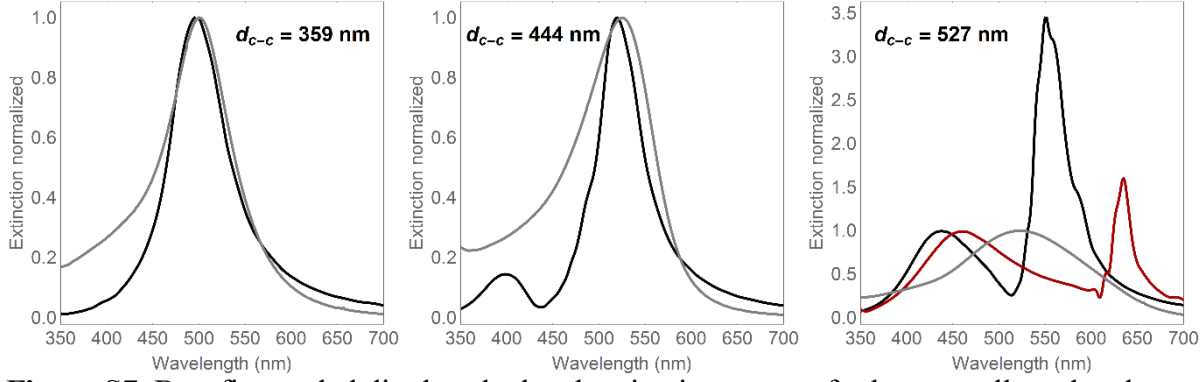


Figure S7. Best fit coupled dipole calculated extinction spectra for hexagonally ordered monolayers, with inter-particle distances $d_{c-c} = 359$, 444 , and 527 nm (as labelled). Calculations with $n_{\text{med}} \approx 1.06$ (black) are compared to experimental absorbance spectra (gray). A high index calculation $n_{\text{med}} \approx 1.3$ (red) is included for $d_{c-c} = 527$ nm to show the effect of the external medium.

The best fit coupled dipole extinction spectra with a radius of 35 lattice sites are shown in Figure S7, with a fit value of $n_{\text{med}} \approx 1.06$. The match is quite good for $d_{c-c} = 359$, reasonable for $d_{c-c} = 444$ nm, and quite poor for $d_{c-c} = 527$ nm. To demonstrate that no match could be found in the last case, we also plot the calculated spectrum for $n_{\text{med}} \approx 1.3$, which results in a different but similarly poor fit.

The mismatch between the coupled dipole calculations and experiment leads us to conclude that dipole interactions are more damped at long inter-particle distances than included in the original model. Therefore we include optical absorption of dipole interactions by assuming a lossy medium. Absorption can be incorporated into the refractive index of the effective external medium through an imaginary part, such that the total (complex) refractive index is now $n_{\text{med}} + i \kappa_{\text{med}}$. The index imaginary part is related to the attenuation coefficient α by $\kappa_{\text{med}} = \lambda_{\text{vac}} \alpha / (4\pi) = \lambda_{\text{vac}} / (4\pi \ell_{\text{atten}})$, where λ_{vac} is the incident light vacuum wavelength and ℓ_{atten} is the characteristic exponential decay length. Optical losses could be the result of several phenomena, including lattice disorder, interference between lattice domains, and inter-particle medium inhomogeneity. The collusion of these effects means that we cannot easily determine the magnitude of the attenuation coefficient from physical intuition. Instead we assume a range of values for α from 0 to $1/(100 \text{ nm})$ and fit the calculated coupled dipole extinction spectra to the experimental spectra to determine the best value. The largest attenuation coefficient corresponds to the radius of the core plus the inner hydrogel shell, essentially recovering a non-interacting monolayer, while the smallest corresponds to infinite range. In addition, we allowed the real part of the medium to vary as before in 0.05 increments, so that our fit is an independent two-parameter fit.

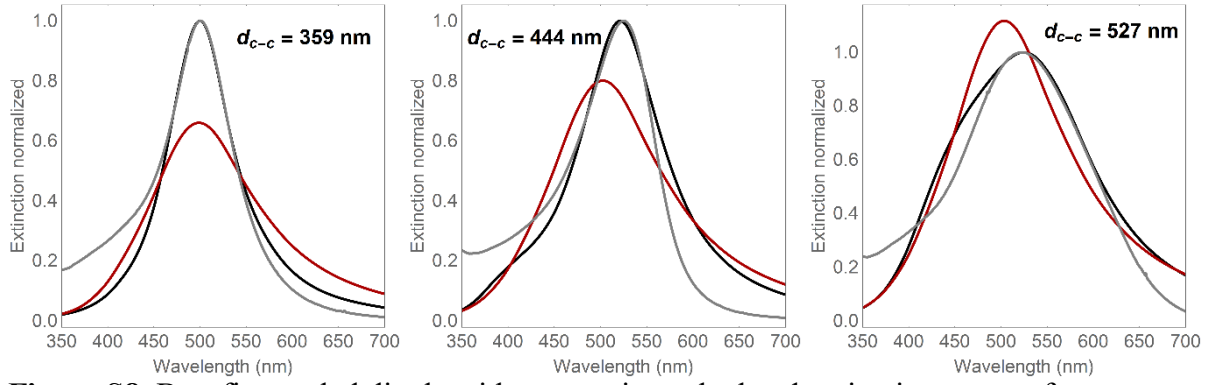


Figure S8. Best fit coupled dipole with attenuation calculated extinction spectra for hexagonally ordered monolayers, with lattice distances $d_{c-c} = 359, 444,$ and 527 nm (as labeled). Calculations with $n_{\text{med}} \approx 1.06$ and $\ell_{\text{atten}} \approx 210$ nm (black) are compared to experimental absorbance spectra (gray). The single particle dipole resonances (red) are also included for comparison. The obtained fit parameters are represented in Figure S9.

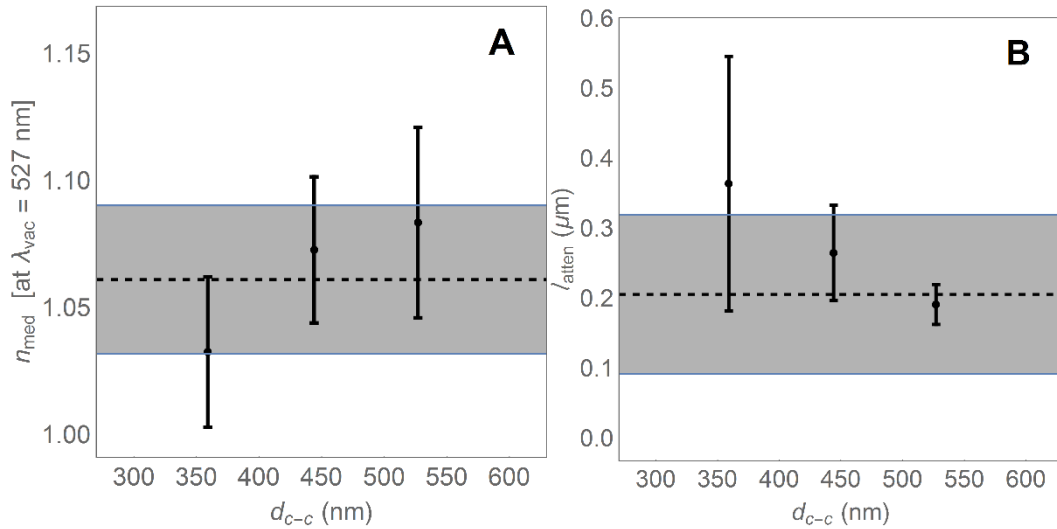


Figure S9. Best fit parameters for the attenuated coupled dipole model. A) Effective medium refractive index n_{med} . B) Characteristic exponential decay length ℓ_{atten} . Overall average values and confidence intervals are represented by dashed traces and gray regions, respectively. Individual confidence intervals are estimated from parameter ranges in the best 5% of fits.

The best fit results for the attenuation length and the refractive index of the external medium are presented in Figure S8 and in the main text, Figure 3D. The calculated and experimental spectra match nicely. The best fit parameters with confidence intervals are plotted in Figure S9. The best fit attenuation length of the smallest inter-particle distance is fairly insensitive, as expected. Taking the mean values from Figure S8A and B, represented by the dashed lines, we calculate the spectra of intermediate inter-particle distances to estimate the effect of inter-particle distance on the plasmonic modes. The results of this survey are presented in Figure S10.

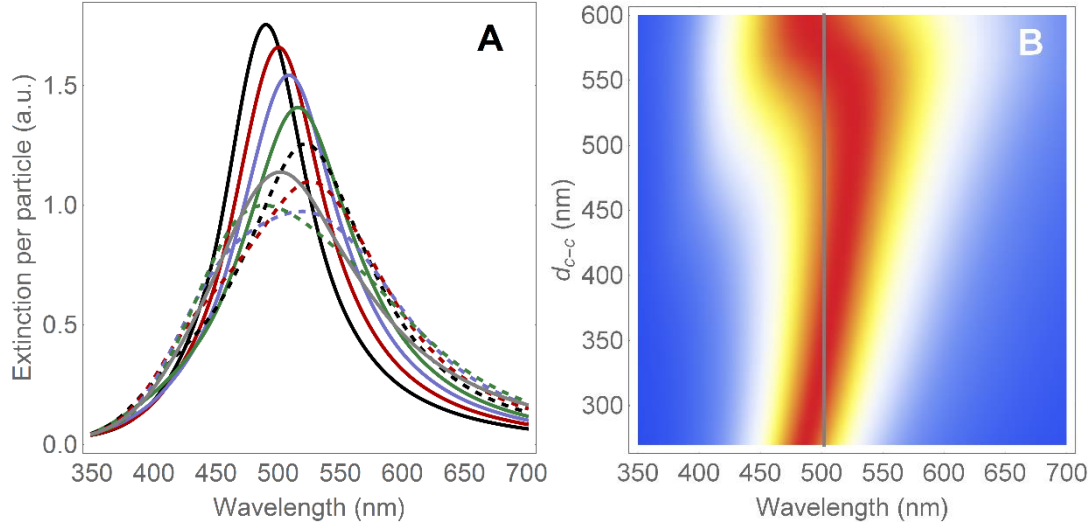


Figure S10. Extinction spectra for varying inter-particle distances d_{c-c} using constant parameters in the attenuated coupled dipole model. Compare to Figure 3 of the main text. A) Extinction spectra with $d_{c-c} = 285$ nm (black), 330 nm (red), 375 nm (blue), 420 nm (green), 465 nm (dashed black), 510 nm (dashed red), 555 nm (dashed blue), and 600 nm (dashed green). The dipole Mie spectrum is also shown (gray). B) Normalized extinction vs d_{c-c} and wavelength, where blue (red) represents low (high) intensity. The maximum of the Mie dipole response is indicated as a gray line.

Random monolayer on glass with coupled dipole approach. Finally, we revisit the random monolayer on glass applying the coupled dipole methods developed for the ordered monolayers in order to better describe that system. In the random monolayer, particles are arranged randomly with an average inter-particle distance of $d_{c-c} = 317 \pm 70$ nm. We generated several different particle configurations with roughly the experimental distances and coverage, with a representative configuration shown in Figure S11A, and fitted the mean extinction spectrum to the experimental data. The best fit spectrum, shown in Figure S11B and in the main text Figure 1, shows a slight improvement over the single-particle approach, in particular producing a narrowing at long wavelengths and a broadening at short wavelengths similar to the experimental spectrum. The best fit parameters are $n_{med} \approx 1.28$ and $\ell_{atten} = 100 \pm 80$ nm. The rapid attenuation here effectively describes interference due to the randomly ordered interactions. The higher medium refractive index may be explained by the rather dense particle packing in this random monolayer and thus a larger hydrogel contribution. However the detailed investigation of the origin of this result are outside the scope of this work.

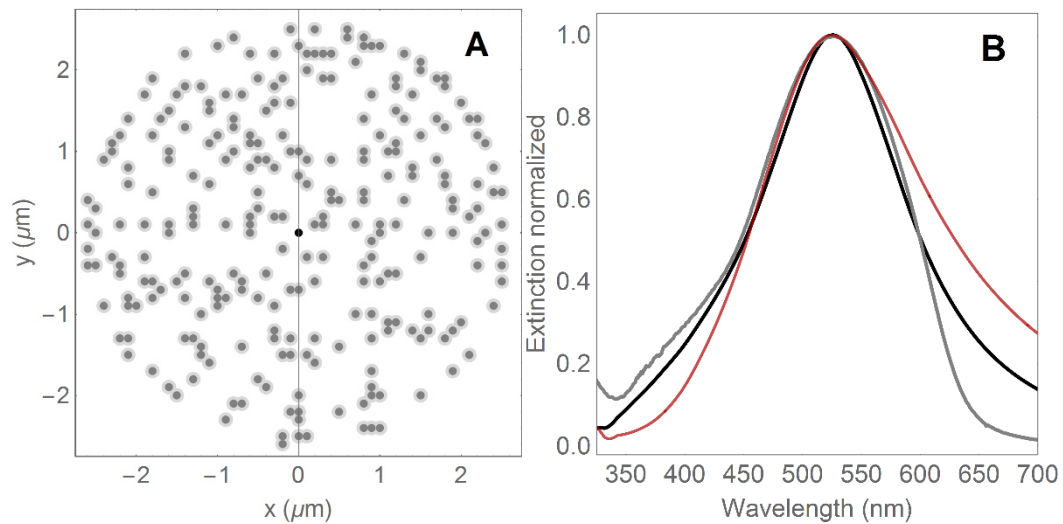


Figure S11. Coupled dipole calculations for a random monolayer. A) A sample particle distribution. B) The average extinction spectrum of several similar configurations calculated with the coupled dipole method is shown in black. For comparison, the experimental absorbance (gray) and single-particle Mie dipole (red) spectra are also plotted.

5 Reversible Tuning of Visible Wavelength Surface Lattice Resonances in Self-Assembled Hybrid Monolayers

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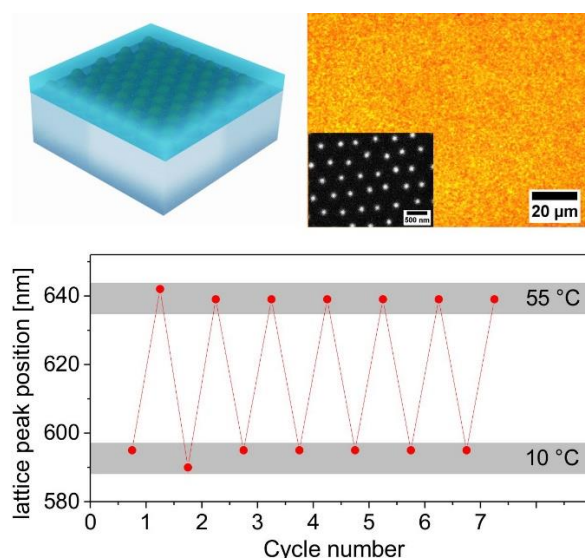
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Keywords: colloidal self-assembly, core-shell particles, nanooptics, resonance tuning, surface lattice resonance



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Next-generation photonic devices require the concentration of electromagnetic energy to subwavelength scales.¹ Gold and silver nanoparticles (NPs) could be ideal candidates for this purpose, due to their ability to support localized surface plasmons (LSPs).² Because of large dephasing, mostly due to non-radiative inter- and intraband excitations, LSPs have broad spectral linewidths.³ This implies short plasmon lifetimes limiting the extensive use of isolated gold and silver NPs in applications like plasmonic nanolasers⁴ and waveguides.⁵ Nanostructures that support low loss plasmons are the focus of intense research in recent years.⁶ While addressing the challenge of narrow linewidths on the single particle level requires the optimization of size, shape and material composition of NPs, a promising concept capitalizing on rather simple building blocks is the arrangement of NPs into periodic arrays. These arrays were found to show narrow surface lattice resonances (SLRs) as result of coupling between LSPs and diffractive modes.⁷ So far, plasmonic arrays supporting SLRs have been fabricated exclusively using lithographic approaches such as electron-beam lithography (EBL)^{7b} and soft interference lithography (SIL).⁸ However, simple and low-cost fabrication methods suitable for large scale applications that create intense electromagnetic fields with dynamic tunability are yet to be developed.⁹ By exchange of the surrounding solvent some tuning of the SLRs has been demonstrated.^{4b, 9} Here, we address a method suitable for fabricating large area devices that support fully reversible, dynamic actuation of SLR modes.

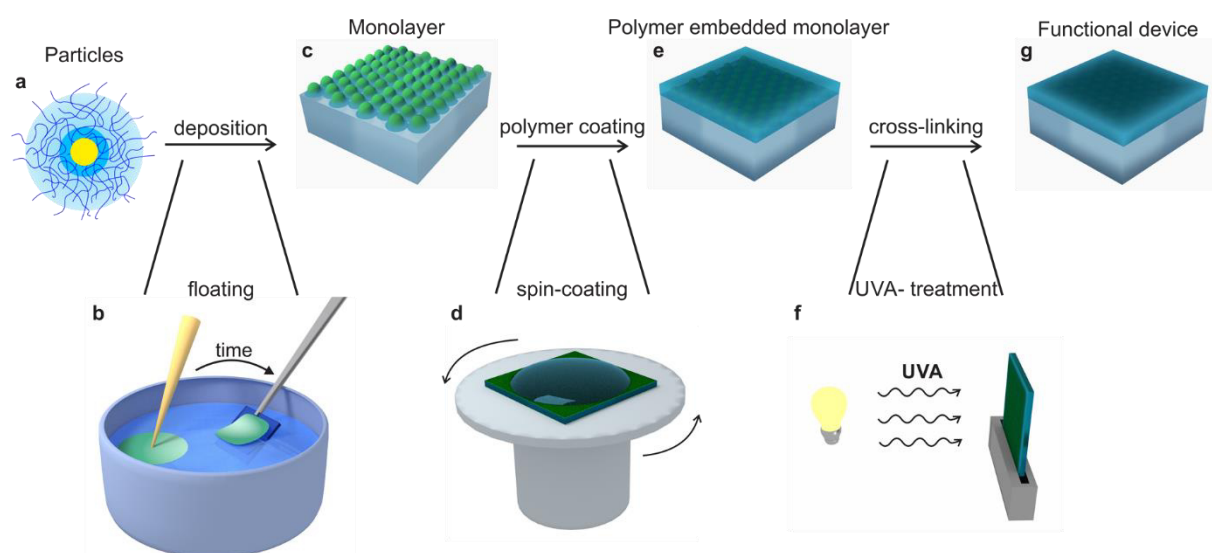


Figure 1. Schematic depiction of the device preparation. Ag@Au-PNIPAM NPs with Ag@Au NC cores and PNIPAM hydrogel shells (a) are employed for the colloidal self-assembly at the air/water interface (b). The freely floating monolayer is transferred to a cm²-sized glass substrate after a certain dwell-time. The resulting hexagonally ordered monolayer of well-spaced Ag@Au NCs (c) is coated with a PNIPAM layer containing benzophenone by spin-coating (d) resulting in a polymer embedded monolayer (e). UVA treatment is used to cross-link the polymer coating (f) forming the final, functional device (g).

We use an array fabrication employing a combination of wet-chemically synthesized hybrid nanoparticles (NPs) and bottom-up self-assembly. cm²-scale hexagonally ordered arrays of silver nanocrystals (NCs) are manufactured. Applying a polymer top layer yields a smart hybrid device supporting pronounced, spectrally narrow SLRs allowing dynamic and fully reversible SLR modulation. The synergistic interplay between the plasmonic NC array and the responsive polymer layer yields a smart, temperature-controllable optical gate. Figure 1 illustrates the device preparation based on colloidal self-assembly of silver@gold-poly-N-isopropylacrylamide (Ag@Au-PNIPAM) core-shell NPs (a). The general assembly concept was adopted from our previous work.¹⁰ The NPs have spherical gold NC cores of 18 nm in diameter with a silver shell leading to an overall diameter of $d_{\text{core}} = 102 \pm 7$ nm. These Ag@Au NCs are encapsulated in a PNIPAM hydrogel shell with a hydrodynamic diameter of $d_h = 326$ nm (at 20°C). A detailed characterization of the structural and optical properties of the core-shell system is given in the works by Honold et al¹⁰ and Dulle et al¹¹. Self-assembly of the NPs at the air/water interface (b) followed by subsequent transfer of the monolayer to a hydrophilic glass substrate resulted in a hexagonal array of well-separated Ag@Au NCs (c).¹² The collected monolayer was dried by applying heat to the substrate in order to firmly adhere the particles to the glass.^{12b} Applying a coating of linear PNIPAM mixed with benzophenone via spin-coating from 1,4-dioxane (d) lead to an optically homogenous environment nearly matching the refractive index (RI) of the glass substrate, $n_{\text{glass}} = 1.52$ (e)^{7a}. A robust device (g) was obtained by photochemically cross-linking the polymer coating with UVA light (f). The resulting polymer matrix is highly cross-linked and strongly bound to the glass substrate.

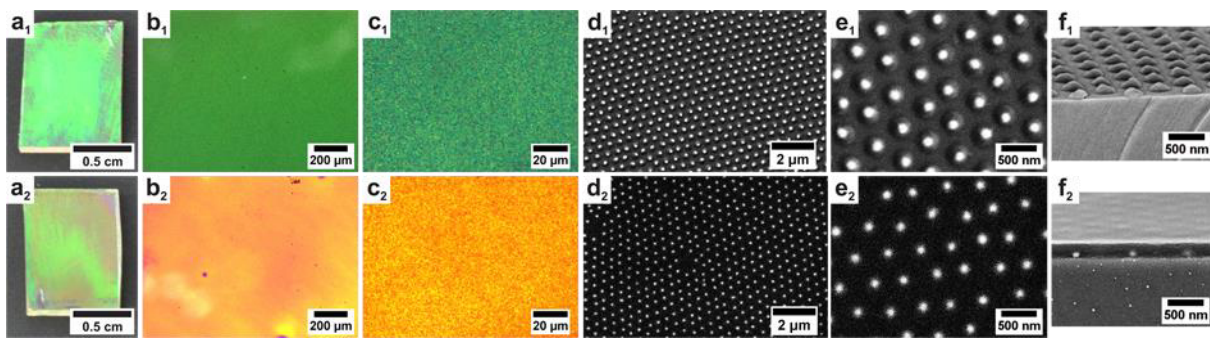


Figure 2. Images of self-assembled Ag@Au arrays investigating cm- to nm-length scales. The NC monolayer on glass (a₁-f₁) is compared to the polymer coated device (a₂-f₂). Digital photographs (a) of the samples (0.8 x 1.2 cm²). Optical microscopy images recorded in bright field mode at low (b) and high (c) magnification. Top-view SEM images at low (d) and high (e) magnification. Side-view SEM images recorded at a tilt angle of 15° (f).

Figure 2 shows the monolayer characteristics from cm- to nm-scale. The images a₁-f₁ correspond to an uncovered sample with an inter-particle distance $d_{c-c} = 455 \pm 28$ nm (compare Figure 1c), while the images a₂-f₂ show a similar sample ($d_{c-c} = 450 \pm 31$ nm) including the

polymer coating (Figure 1g). The digital photographs (a) demonstrate the macroscopic dimensions of the prepared samples, here $0.8 \times 1.2 \text{ cm}^2$. Optical microscopy images at low (b) and high magnification (c) emphasize the homogeneity as evidenced by the regular color. The granular structure visible in the higher magnification images (c) is related to individual single crystalline domains. It is important to note that the different colors (green and orange) of the uncoated (b_1, c_1) and coated (b_2, c_2) samples are a consequence of the different resonance modes. Supplementary Figure S1 supports this, showing an optical microscopy image obtained from a polymer coated sample which has been partially treated by an electron beam removing the polymer coating. The polymer coated sample area appears orange while the electron beam treated area appears green. We attribute this change in color to the selective removal of the polymer overcoating. The large single-crystalline domains and the regular hexagonal packing of the Ag@Au NCs is seen by SEM (Figure 2d,e). The regular inter-particle distances are a result of the hydrogel shell that acts as a semitransparent, dielectric spacer between the plasmonic cores.¹⁰ Comparing the SEM images of the uncoated (Figure 2d₁,e₁) and coated (Figure 2d₂,e₂) samples, it is evident that the monolayer order is not affected by the application of the coating. Figure 2f shows cross-sectional SEM images of the uncoated and coated samples, demonstrating the smoothness of the polymer layer embedding the NC monolayer. Atomic force microscopy (AFM) images obtained from all monolayers relevant to this work along with Fast Fourier Transforms of the images can be found in the Supplementary information (Figure S2 and S3).

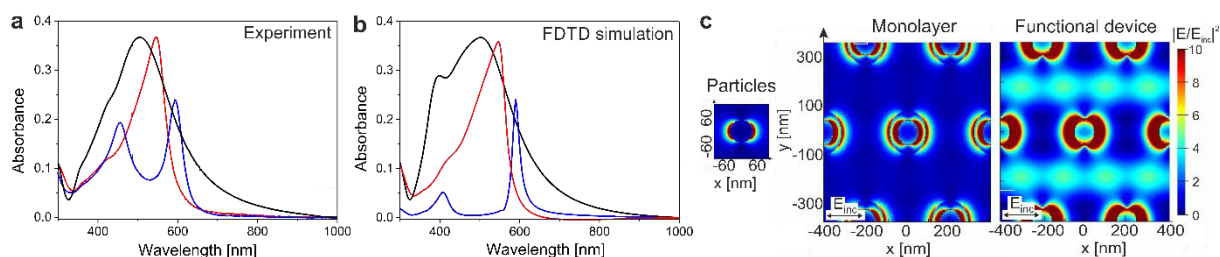


Figure 3. Optical properties of Ag@Au NC arrays. Experimental UV-vis spectra (a) show a single LSPR at 505 nm for particles in aqueous dispersion (black trace, normalized to maximum absorbance of monolayer on glass), a significantly narrowed and red-shifted LSPR at 550 nm for a hexagonal NC array on glass with $d_{c-c} = 419 \text{ nm}$ (red trace), and two distinct peaks at 455 and 594 nm for the NC array covered in a cross-linked PNIPAM top-layer (blue trace). Spectra obtained from FDTD calculations (b) with the same color-coding as in (a). Near-field electromagnetic intensity ($|E/E_{inc}|^2$) maps from FDTD simulation (c) of the particles in water, in an array on glass (Monolayer) and in the functional device at the SLR ($\lambda_{SLR} = 594 \text{ nm}$).

Figure 3 compares experimental (a) extinction spectra from different stages of device preparation to simulated (b) spectra calculated from finite-difference time-domain (FDTD). A dilute aqueous dispersion ($n_{H_2O} = 1.33$) of the Ag@Au-PNIPAM NPs (black spectra), which is

representative of the uncoupled colloidal building blocks, shows a broad (FWHM = 200 nm) LSPR at $\lambda_{\text{LSPR}} = 505$ nm. Upon assembly of the NPs into an ordered monolayer (Figure 1c), a much narrower (FWHM = 100 nm) and red shifted (to 545 nm) resonance is measured, in good agreement with the FDTD computations (red spectra). The pronounced reduction in linewidth is due to weak dipole-dipole coupling between NCs in the monolayer^{12b}. This coupling remains weak due to the inhomogeneous RI environment with contributions from the glass substrate, the collapsed PNIPAM shells and air (Figure 1c). Following an experimental report by Auguie *et al.*,^{7a} we next covered the sample with polymer in order to make the RI environment more homogeneous. Strikingly, the final device shows two narrow and well-separated peaks at 455 nm and 594 nm (blue spectra). These resonances are a result of strong coupling that is only possible with the homogeneous RI environment (Figure 1e). While the essential mechanism explaining the critical role of the homogeneous RI is illusive, it appears that interference between scattering by the plasmonic nanoparticles and reflection at the glass layer may play a critical role.¹³ The peak at 594 nm has a FWHM = 43 nm leading to a Q-factor of $Q = \lambda/\Delta\lambda = 13.8$. This is an increase in Q of more than five times as compared to the LSPR of the particles in dilute dispersion. This peak position and linewidth are in remarkably good agreement with the predictions of an early theoretical work which modeled a very similar system of spherical Ag nanoparticles with a diameter of 100 nm arranged in hexagonal arrays in air.^{7f} Using finite-sized crystalline domains, that study gave peak widths in the range of 20–40 nm ($Q = 10$ –20). These quality factors are lower than devices with larger inter-particle distances which support infrared resonances due to the larger optical losses in the visible.^{4c} Likewise, the FDTD calculations (blue spectrum, Figure 3b) are in good qualitative agreement with the experimental spectra. However, there are deviations in the peak positions and peak strengths. These deviations are mostly related to differences between our experimental monolayer structure (deviation in d_{c-c} , finite domain size, more complex local refractive index environment) and the perfect hexagonal array used for the FDTD calculations. Insight into the electromagnetic structure of these resonances is provided by the near-field maps from FDTD simulation shown in Figure 3c. For isolated NPs dispersed in water, the near-fields are dominated by the dipolar LSPR. In the periodic monolayer, the dipolar fields are still the primary contribution, although they are scattered at the air-polymer shell interface. In contrast, the final device exhibits a pronounced lattice mode at 594 nm with a (1,0) diffraction mode structure, consistent with a SLR.

The shorter wavelength resonance peak ($\lambda = 455$ nm) in the spectra of Figure 3a,b points to dipole coupling to higher order lattice modes. In the following we will focus on the investigation

of parameters influencing the position and strength of the higher wavelength peak that can be clearly assigned to a SLR. To our knowledge, this is the first report of SLRs in self-assembled, macroscopic arrays of wet-chemically synthesized plasmonic NCs.

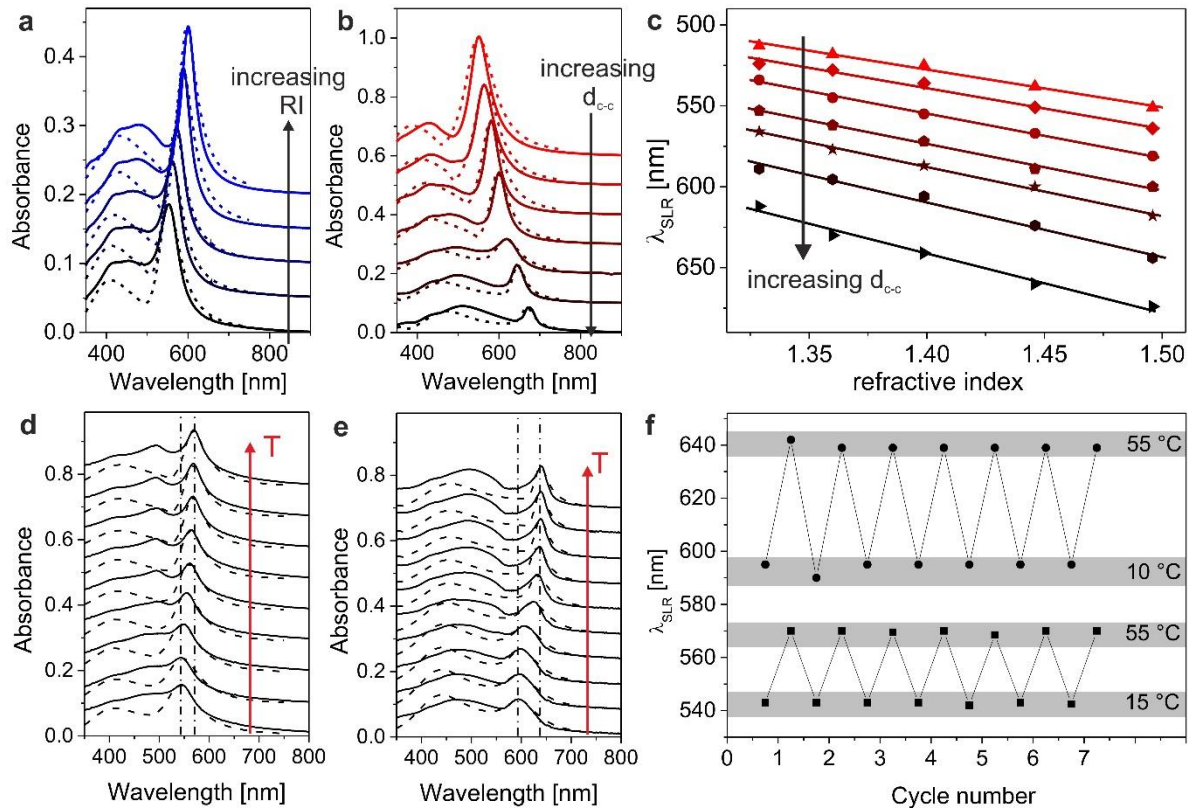


Figure 4. Influence of solvent refractive index, lattice spacing and temperature on SLR peak position. Evolution of the absorbance spectra of a PNIPAM-coated NC array with $d_{c-c} = 419$ nm immersed in different solvents (a), from bottom to top: methanol ($n = 1.33$), ethanol ($n = 1.36$), butanol ($n = 1.40$), chloroform ($n = 1.45$) and toluene ($n = 1.50$). Results from measurements in toluene ($n = 1.50$) in dependence of d_{c-c} (b), from bottom to top: $d_{c-c} = 506, 474, 419, 407, 374$, and 356 nm. Solid lines are experimental results and dashed lines correspond to the respective results from theoretical CDA computations. The spectra have offsets in steps of 0.1. Refractive index dependence of experimentally determined SLR peak positions (symbols) (c). Solid lines are linear fits to data for each lattice spacing (bottom to top: $d_{c-c} = 506, 474, 419, 407, 374$, and 356 nm). Experimental absorbance spectra for PNIPAM-coated NC arrays measured in water at different temperatures (d, e). NC array with $d_{c-c} = 430$ nm starting at 15°C (bottom to top) with temperatures increasing in steps of 5°C up to 55°C (d). NC array with $d_{c-c} = 488$ nm starting at 10°C (bottom to top) with temperatures increasing in steps of 5°C up to 55°C (e). Solid lines are experimental data and dashed lines show results from computations using CDA. Experimental reversibility study on SLR tuning of the two devices with $d_{c-c} = 430$ nm (squares) and $d_{c-c} = 488$ nm (circles) (f).

The SLR energy can be fine-tuned by immersing a device ($d_{c-c} = 419$ nm) into solvents with a range of RIs, as demonstrated in Figure 4a. The solvents can fully infiltrate the cross-linked PNIPAM coating. The absorbance spectra obtained by a stepwise increase of RI from methanol ($n = 1.33$), ethanol ($n = 1.36$), butanol ($n = 1.40$), chloroform ($n = 1.45$) to toluene ($n = 1.50$) show peak

shifts from 553 nm to 600 nm, while maintaining a narrow linewidth (FWHM = 40-50 nm). The observed shift of the SLR closely follows the (1,0) diffraction mode that shifts from 483 nm to 585 nm as the RI of the environment is increased from 1.33 to 1.50. For future applications the demonstrated infiltration by solvent can also be used to infiltrate the monolayer with analytes, e.g. for sensing applications. Due to the porous structure of the PNIPAM network the accessibility of the metal cores is still guaranteed.

The soft and deformable character of the PNIPAM hydrogel shell allowed for the fabrication of monolayers with inter-particle distances that can be easily tuned by the dwell-time of the monolayer at the air/water interface, producing arrays with spacings from $d_{c-c} \approx d_h$ nm to $d_{c-c} \approx 1.6d_h$ ^{12b}. This provides easy access for a systematic study of the coupling strength, i.e. the SLR position and intensity, as a function of inter-particle spacing. Figure 4b shows that the SLR peak shifts to lower wavelength for decreasing d_{c-c} and the coupling becomes stronger. For large values of d_{c-c} the LSPR at lower wavelength ($\lambda_{LSPR} = 505$ nm) significantly contributes to the spectra, underlining the weaker coupling. The extinction spectra in Figure 4a,b are nicely reproduced with calculations using the coupled dipole approximation (CDA)^{7c, 14}. Additional spectra from experiment and CDA simulation for samples with different d_{c-c} as a function of solvent RI can be found in Figure S4. Figure 4c combines the results from Figure 4a, Figure 4b and Figure S4. The smallest lattice spacing of 356 nm exhibits the smallest SLR wavelength shift, from 513 nm to 551 nm ($\Delta\lambda = 38$ nm). The largest spacing of $d_{c-c} = 506$ nm exhibits greatly red shifted SLR positions, from 612 nm to 674 nm, and enhanced tuning, $\Delta\lambda = 62$ nm. The tuning behavior of the resonance modes is another indicator for the diffractive/plasmonic coupled nature of our SLRs. The diffraction mode position is proportional to the RI and the lattice spacing ($\lambda \sim n \cdot d_{c-c}$). Consequently we expect the SLR shift in response to a RI change to be proportional to the lattice spacing ($\Delta\lambda/\Delta n \sim d_{c-c}$). Hence, the same change in RI relates to a more pronounced SLR shift for increasing d_{c-c} , in good agreement with our findings. This study shows that a single batch of core-shell NPs in combination with a simple self-assembly protocol can be employed to produce samples with distinct SLRs in a range of wavelength as large as 513 - 674 nm ($\Delta\lambda = 161$ nm). This is possible just by variation of the dwell-time before monolayer transfer, i.e. the lattice spacing, and the RI of the immersing solvent.

In order to create a smart device that can be dynamically tuned with a practically more relevant trigger than solvent exchange, we decided to exploit the temperature responsiveness of PNIPAM. At temperatures above 32-33°C PNIPAM collapses in water, increasing the polymer density and RI of the top layer. The exact switching temperature depends on the degree of

crosslinking and its chemical nature.¹⁵ This volume phase transition behavior allows us to change the RI environment in an easy, non-destructive manner by simple variation in temperature. Due to the chemical cross-linking of the polymer coating to the core-shell particles, which are firmly attached to the glass substrate, swelling and deswelling can only occur along the *z*-axis of the sample. Therefore, the lattice spacing is not affected by the temperature change and the consequent collapse of the polymeric layer. Figure 4d-f shows the influence of temperature on samples with $d_{c-c} = 430$ nm (d) and $d_{c-c} = 488$ nm (e). The sample with smaller d_{c-c} (d) shows a SLR shift from 543 nm to 570 nm ($\Delta\lambda = 27$ nm), while the larger d_{c-c} sample (e) shows a shift from 595 nm to 639 nm ($\Delta\lambda = 44$ nm). An exemplary temperature cycle in 5°C increments from 10°C to 55°C for the larger d_{c-c} sample is shown in the SI in Figure S5. The SLR positions nearly perfectly overlap between the heating and the cooling curve without any indication for a hysteresis. From the CDA calculations (dashed lines) and comparison to the results shown in Figure 4c, we determine a change in RI from 1.33 to approximately 1.45 through the temperature induced collapse of the PNIPAM layer. These RI values agree well with a highly swollen PNIPAM film with an index close to water ($n = 1.33$) at 10/15 °C and a collapsed PNIPAM with a much higher polymer density and hence an index closer to that of the pure polymer ($n = 1.48$) at 55 °C.^{12b} Evaluating the fits from CDA calculations the swollen polymer state corresponds well to the static device in methanol. With a spacing of $d_{c-c} = 488$ nm for the larger spaced sample the spacing lies in between the static samples with $d_{c-c} = 474$ and $d_{c-c} = 507$ nm and also the SLR of 595 nm is in between 589 nm and 506 nm of the static devices in methanol. This supports the assumption that the highly swollen polymer film leads to roughly the same RI as pure methanol of 1.33. Studying the collapsed state at elevated temperatures the SLR of 639 nm for the larger spacing gave an RI of 1.45 when fitting with the CDA method. This corresponds to a polymer film with 20 % residual water and also to the static sample in chloroform. In chloroform SLRs of 624 nm and 660 nm were obtained with spacings of $d_{c-c} = 474$ nm and $d_{c-c} = 508$ nm, respectively. Our device with an SLR of 639 nm lies again within those values. Considering the tuning range this also fits well considering the shifts of $\Delta 35$ nm, $\Delta 44$ nm and $\Delta 48$ nm going from $d_{c-c} = 474$ nm, 488 nm and 508 nm. With this comparison a good correlation between temperature increase and RI increase can be qualitatively shown. Figure 4f demonstrates the SLR tuning is fully reversible over 7 heating/cooling cycles without any evidence for depletion, for example because of device degradation. An even more extended study on the reversibility of the swelling and deswelling behavior with 20 temperature cycles is shown in the SI in figure S6 with a comparable sample. In order to exclude movements of the particles in the polymeric layer in

the swollen state, which could lead to a change/tuning in the LPR positions, AFM measurements were performed in a liquid cell in water. Figure 5 shows a monolayer on glass (a), the same monolayer covered with crosslinked and swellable PNIPAM in the dry (= collapsed) state (b) and when immersed into room temperature water in the swollen state (c). The uncoated monolayer shows an interparticle spacing of $d_{c-c} = 511 \pm 27$ nm, the same spacing was obtained for the coated dry device $d_{c-c} = 512 \pm 18$ nm and also for the coated swollen device $d_{c-c} = 511 \pm 55$ nm. The measurement in water shows a lower resolution due to the changed sample environment, the less defined and less corrugated top layer of the coating due to swelling. Nevertheless the particle positions remains stable with only the error bar increasing from 27 to 55 nm due to more difficult imaging conditions.

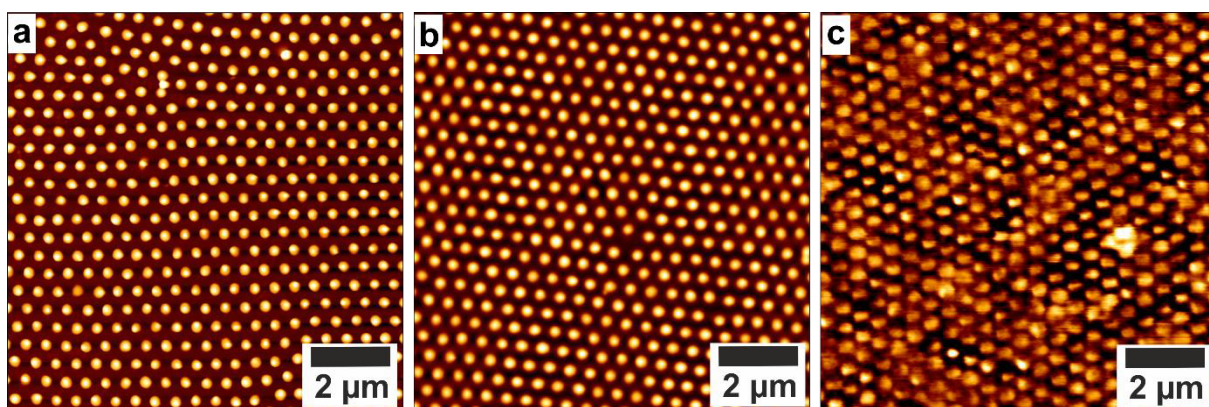


Figure 5. Influence of polymer coating and aqueous environment on particle spacing. AFM image of an uncoated monolayer with $d_{c-c} = 511 \pm 27$ nm (a), of the same sample with PNIPAM coating in air $d_{c-c} = 512 \pm 17$ nm (b) and the device immersed into water at room temperature $d_{c-c} = 511 \pm 55$ nm (c).

In summary, we have provided the first example of SLRs in self-assembled monolayers of wet-chemically synthesized plasmonic NCs. Our lithography-free method is scalable and allows for the facile fabrication of macroscopically coated substrates. The resonance of the SLR strongly depends on the inter-particle spacing d_{c-c} and the refractive index of the surrounding environment. In addition, we have demonstrated a new concept of dynamic tuning of the SLR energy in a non-destructive manner in a smart hybrid device. Employing temperature as a reversible trigger to adjust the SLR position, the spectral overlap of the device SLR with other optical modes can be varied. This opens the pathway for dynamic interactions with optically active materials, such as dyes or quantum dots. This new concept may even result in advanced logical photonic components such as switchable nanoscale light sources. Using laser heating of the plasmonic NCs may lead to a local variation of temperature. Consequently, the SLR mode could tune in and out of the absorption resonance leading to a self-regulating optical filter.

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Supporting Information

Wet-chemical synthesis of Ag@Au-PNIPAM core-shell particles

Gold (III) chloride trihydrate (Sigma-Aldrich, $\geq 99.9\%$), sodium citrate dihydrate (Aldrich, $\geq 99\%$), sodium dodecylsulfate (SDS; Merck), butenylamine hydrochloride (BA; Sigma-Aldrich, 97%), *N*-Isopropylacrylamide (NIPAM; Sigma-Aldrich 97%), *N,N'*-methylenebisacrylamide (BIS; Fluka, $\geq 98\%$) potassium peroxodisulfate (PPS; Fluka, $\geq 99\%$), L-ascorbic acid (Sigma Aldrich, reagent grade), ammonium hydroxide solution (Sigma-Aldrich, 30-33%), ethanol abs. (VWR Chemicals, 99.1-100%), glycine (Merck, $\geq 99.7\%$), hexadecyltrimethylammonium bromide (Fluka, $\geq 96.0\%$), silver nitrate (Fluka, puriss. p.a. $\geq 99.5\%$), sodium hydroxide (Grüssing, 1 M), 1,4-Dioxane (Merck, $\geq 99.5\%$), and benzophenone (Acros organics, 99% pure) were used as received. Purified water from a Milli-Q system (Millipore) with a final resistivity of 18.2 M Ω cm was used for all synthesis, purification and assembly steps. All glassware were cleaned using aqua regia and thoroughly rinsed with water, acetone and ethanol.

Gold nanoparticles of 18 nm in diameter (as determined from TEM) were prepared by the well-known method of Turkevich using citrate as reducing agent.¹ Briefly, 200 mL of 5×10^{-4} M HAuCl₄ were heated until heavy boiling while being continuously stirred. Then, 10 mL of a preheated aqueous solution of trisodium citrate (0.67 wt%) were added quickly and boiling was continued for 20 min. Afterwards the deeply red gold nanoparticle dispersion was allowed to cool to room temperature. 1.2 mL of a 0.624 mM aqueous SDS solution were added to the gold particle dispersion at room temperature. After 20 min of stirring following the SDS addition, 0.392 mL of a 2.88 mM butenylamine hydrochloride solution in ethanol were added dropwise and stirring was continued for 20 min. Finally, the gold nanoparticles were concentrated by four centrifugation steps for 90 min at 3300 rcf. The residues were collected and stored in the dark at room temperature.

The functionalized gold nanoparticles were encapsulated into hydrogel shells by seeded precipitation polymerization.² A total of 100 mL of water containing 0.02 M NIPAM and 15 mol% of BIS (referred to the monomer) were mixed in a three-neck round bottom flask (250mL) and heated to 70 °C using an oil bath and a magnetic stirrer. Additionally, the flask was equipped with a reflux condenser. The reaction solution was degassed with nitrogen for 30 min. Afterwards, 2.35 mL of the functionalized gold particles in water ([Au] = 0.01 M) were added dropwise. After 15 min of equilibration time, the polymerization was started by the rapid addition of 2 mg of potassium peroxodisulfate dissolved in 1 mL of water. The red and clear particle dispersion became slightly turbid within the first 15 min of reaction time. Two hours after the addition of the initiator, the dispersion was allowed to cool down to room temperature.

Cleaning of the Au-PNIPAM core-shell hybrid particles was carried out by repeated centrifugation (90 min at 6500 rcf) and redispersion in water. Three steps of centrifugation and redispersion were performed. Finally, the particles were concentrated to an aqueous dispersion of 2 wt%.

Overgrowth of the gold cores of the Au-PNIPAM particles was done using a seeded-growth protocol.³ 6.00 g of glycine (80 mmol) and 3.64 g of CTAB (10 mmol) were dissolved in 200 mL of MQ water at 35 °C. After the solution was cooled to room temperature, 1 mL of an Au-PNIPAM dispersion (2 wt%) was added. Next 16 mL of a 0.1 M NaOH solution were added, followed by the addition of 9 mL of an ascorbic acid solution (100 mM). Then 13.1 mL of a freshly prepared AgNO₃ solution (15 mM), which was kept in the dark, were added stepwise to the reaction mixture (655 μ L every two minutes). Stirring was continued for 20 minutes after the last addition. The reaction mixture was diluted with MQ water and centrifuged (1 h at 3740 rcf). This process was repeated two times using MQ water, two times with ethanol and again two times with MQ water for redispersion of the residues. After the last cleaning step, the collected residues were redispersed in ethanol to yield dispersions of Ag@Au-PNIPAM particles with 2 wt % solid contents.

Monolayer and device preparation

The NP assembly at the air/water interface and the subsequent transfer of the freely floating monolayer was performed as previously described by us.⁴ A crystallization dish was filled with MilliQ water. Then, 10 μ L of the dispersion were carefully transferred to the air/water-interface using an Eppendorf pipette. Immediately, a freely-floating particle monolayer formed at the interface as evidenced by strong opalescence. The monolayer was transferred on hydrophilic glass slides by immersion of the glass slide into the floating bath and retraction of the glass slide at a shallow angle with the monolayer sticking to the substrate. Drying of the monolayer was accelerated by a heat-gun blowing to the back of the substrate. We found that this step also helps to attach the particles more firmly to the glass, enabling spin-coating of a polymeric layer on top of the monolayer.

The final device was fabricated by spin-coating of 40 μ L of a solution containing 25 (40) mg linear PNIPAM (40 000 g/mol, synthesized according to Ebeling *et al.*⁵) and 10 mg Benzophenone (3.3 mg) in 1 mL 1,4-Dioxane at 2000 rpm for 30 s resulting in a polymer layer of 150 (280) nm thickness. The values in parentheses correspond to samples made for temperature dependent measurements in water (Figure 4 d-f). The polymer coatings were cross-

linked for 1 h with UVA irradiation (Hönle UV F 400F, 400W, blue filter: 320 nm – 420 nm, $T < 30^{\circ}\text{C}$).

Scanning electron microscopy (SEM)

SEM analysis was carried out by a field-emission scanning electron microscope (Ultraplus, Zeiss, Germany) using acceleration voltages between 2 and 5 kV. The images were taken with an InLens SE detector (Fig. 2d₁,e₁), an Everhart-Thornley SE detector (Fig. 2d₂,e₂) as well as with an energy selective backscattered (EsB) detector (Fig. 2f₁,f₁) to enhance the material contrast.

Optical microscopy

The optical microscopy images were captured in bright-field mode using an Axio Imager.A2m (Zeiss, Germany) equipped with a motorized stage and a digital camera AxioCam ICc 1.

Optical microscopy analysis of polymer coated device

Figure S1 shows a low-magnification optical microscopy image captured in bright-field mode. The image shows a device ($d_{c-c} = 450\text{ nm}$) that has been partially treated with an electron beam removing the polymer top layer. The polymer-coated sample area appears orange. The treated area, where the polymer has been removed, appears green.

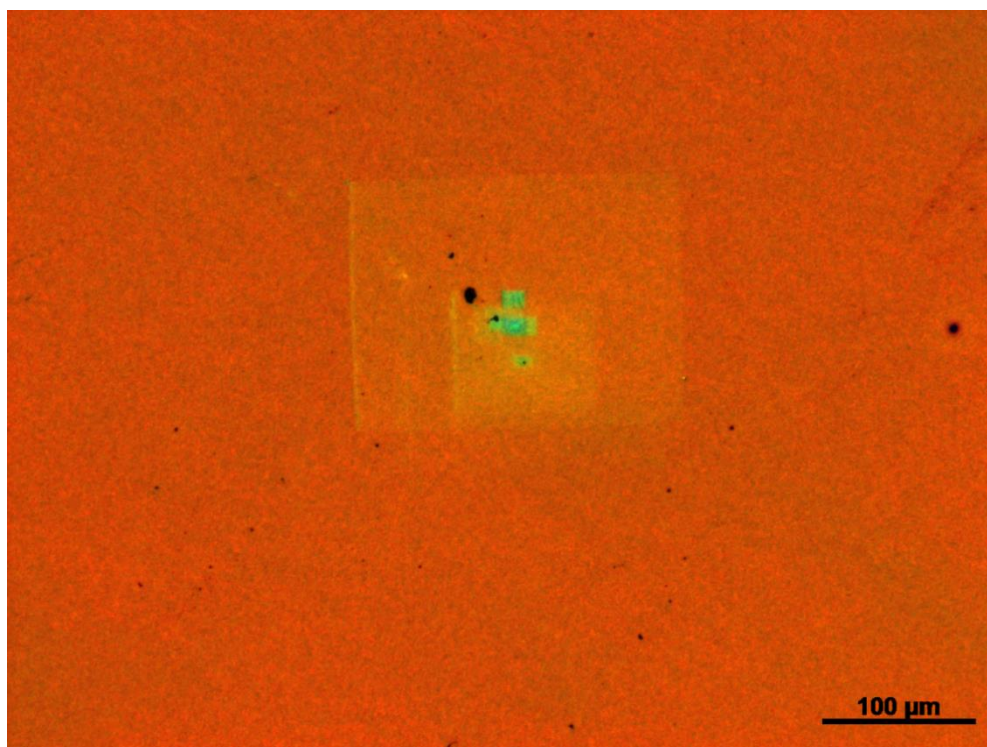


Figure S1. SEM image of PNIPAM-coated Ag@Au-PNIPAM monolayer (orange) which has been partially treated by an electron beam removing the polymer coating. The untreated sample area appears orange while the electron beam treated area appears green.

Atomic force microscopy

10×10 μm^2 topographic AFM images were recorded with a Nanoscope Multimode AFM (Veeco) in tapping mode against air. OTESPA-R3 AFM probes (Bruker) were employed for image recording. The cantilevers possess a resonance frequency of approximately 300 kHz and a spring constant of approximately 26 N/m. The tip geometry was a visible apex with a nominal tip radius of 7 nm.

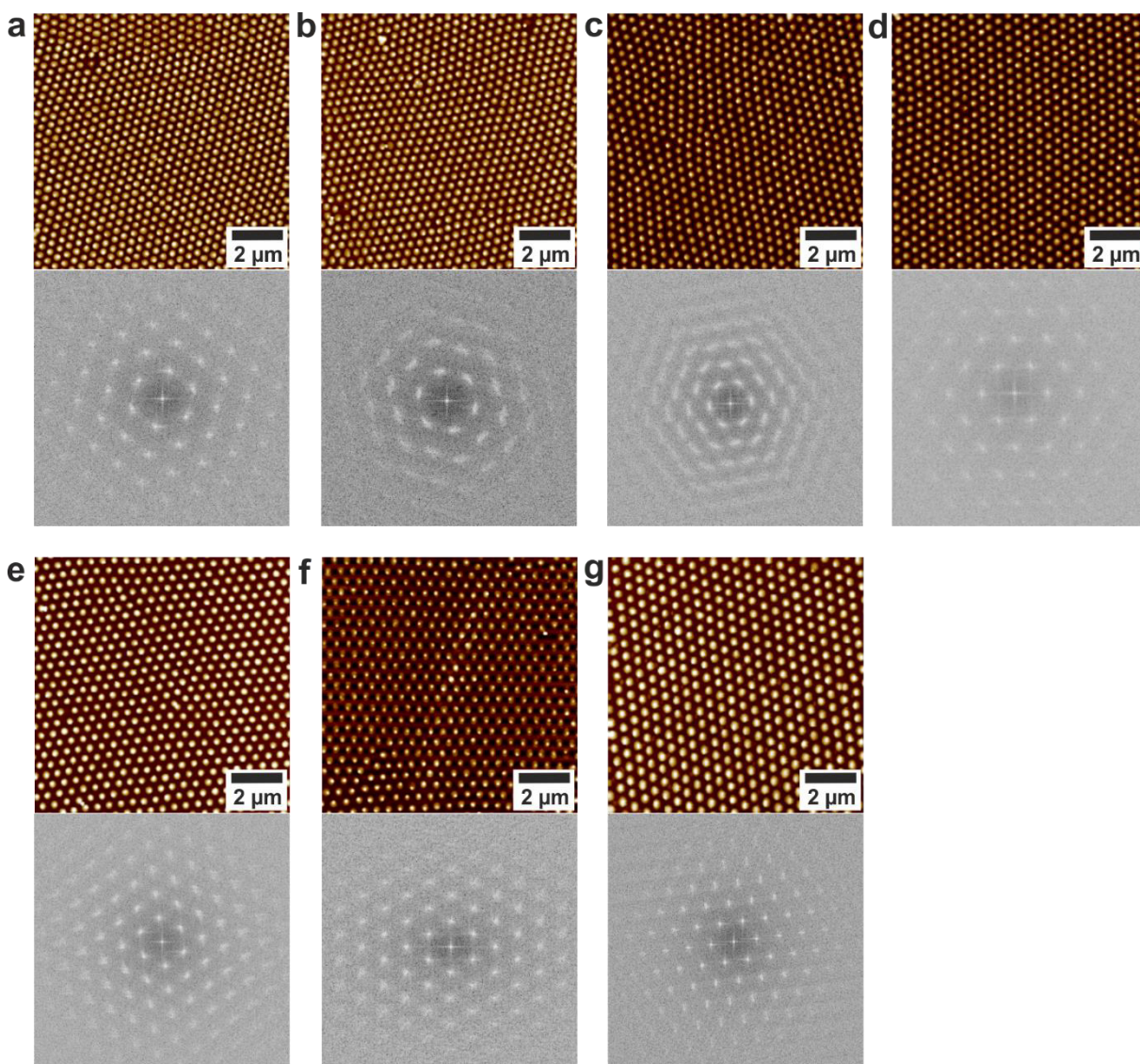


Figure S2. Monolayer structure of devices for refractive index dependent experiments. AFM images and Fast Fourier Transforms (FFTs) of all particle monolayers used for devices in solvent exchange experiments. The images correspond to monolayers with $d_{c-c} = 356$ nm (a), $d_{c-c} = 374$ nm (b), $d_{c-c} = 407$ nm (c), $d_{c-c} = 419$ nm (d), $d_{c-c} = 451$ nm (e), $d_{c-c} = 474$ nm (f), and $d_{c-c} = 506$ nm (g).

Figure S2 shows AFM height profiles of monolayers withdrawn after different dwell-times at the air/water interface resulting in inter-particle distances of $d_{c-c} = 356$ nm (a), $d_{c-c} = 374$ nm (b), $d_{c-c} = 407$ nm (c), $d_{c-c} = 419$ nm (d), $d_{c-c} = 451$ nm (e), $d_{c-c} = 474$ nm (f), and $d_{c-c} = 506$ nm (g).

(g). The pronounced hexagonal order with large single-crystalline domains is supported by the accompanied Fast Fourier Transforms (FFTs) of the images. The inter-particle distances d_{c-c} were calculated from pair-correlation functions $g(r)$ determined from the AFM images.

Figure S3 shows AFM height profiles of monolayers that were used for the preparation of devices for our temperature dependent experiments in water. The inter-particle distances are $d_{c-c} = 430$ nm (a) and $d_{c-c} = 488$ nm (b).

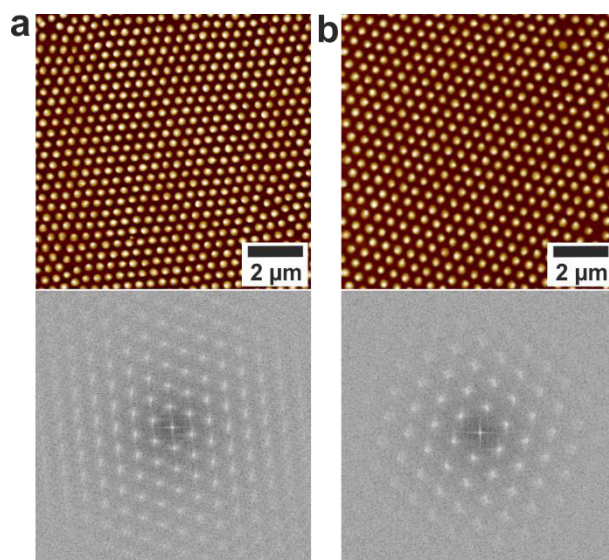


Figure S3. Monolayer structure of devices for temperature dependent experiments. AFM images and Fast Fourier Transforms (FFTs) of particle monolayers with $d_{c-c} = 430$ nm (a) and $d_{c-c} = 488$ nm (b).

Extinction measurements

Extinction measurements were performed with an Agilent 8453 UV-vis spectrometer equipped with a temperature-controlled sample holder. The temperature was adjusted with a circulating water bath (Julabo F30-C). Spectra were recorded in a wavelength range of 190 nm to 1100 nm in transmission geometry. Spectra of particle dispersions and of the devices in water, methanol, ethanol, butanol, chloroform and toluene were recorded in 1×1 cm² quartz glass cuvettes closed with Teflon stoppers. The devices were placed upright in the cuvettes filled with solvent. All spectra were background and substrate corrected and converted into absorbance spectra.

Uncoupled nanoparticle absorption spectrum. The black traces in Figure 3 compare experimental (a) extinction spectrum of individual core-shell nanoparticles in aqueous dispersion to a simulated (b) spectrum calculated from FDTD. A dilute aqueous dispersion ($n_{H_2O} = 1.33$) of the Ag@Au-PNIPAM NPs (black spectra) shows a broad (FWHM = 200 nm) LSPR at $\lambda_{LSPR} = 505$ nm. The weak shoulder at approx. 400 nm can be attributed to a small quadrupolar contribution. The experimental quadrupole is weaker than theoretically expected.

This is related to the shape of the Ag@Au NCs, deviating slightly from perfect spheres with crystal planes at the particle surface.

Influence of inter-particle distance and solvent refractive index on SLR position. Figure S4 shows UV-vis absorbance spectra recorded for devices with different inter-particle distances as a function of solvent refractive index. Each graph shows experimental spectra (solid lines) of one device for five different solvents. The refractive index increases from bottom to top: Methanol ($n = 1.33$, black trace), ethanol ($n = 1.36$), butanol ($n = 1.40$), chloroform ($n = 1.45$) and toluene ($n = 1.50$). All samples show a shift of the SLR towards longer wavelengths for increasing refractive index. The inter-particle distances of the devices are: $d_{c-c} = 356$ nm (a), $d_{c-c} = 374$ nm (b), $d_{c-c} = 407$ nm (c), $d_{c-c} = 419$ nm (d), $d_{c-c} = 451$ nm (e), $d_{c-c} = 474$ nm (f), and $d_{c-c} = 506$ nm (g).

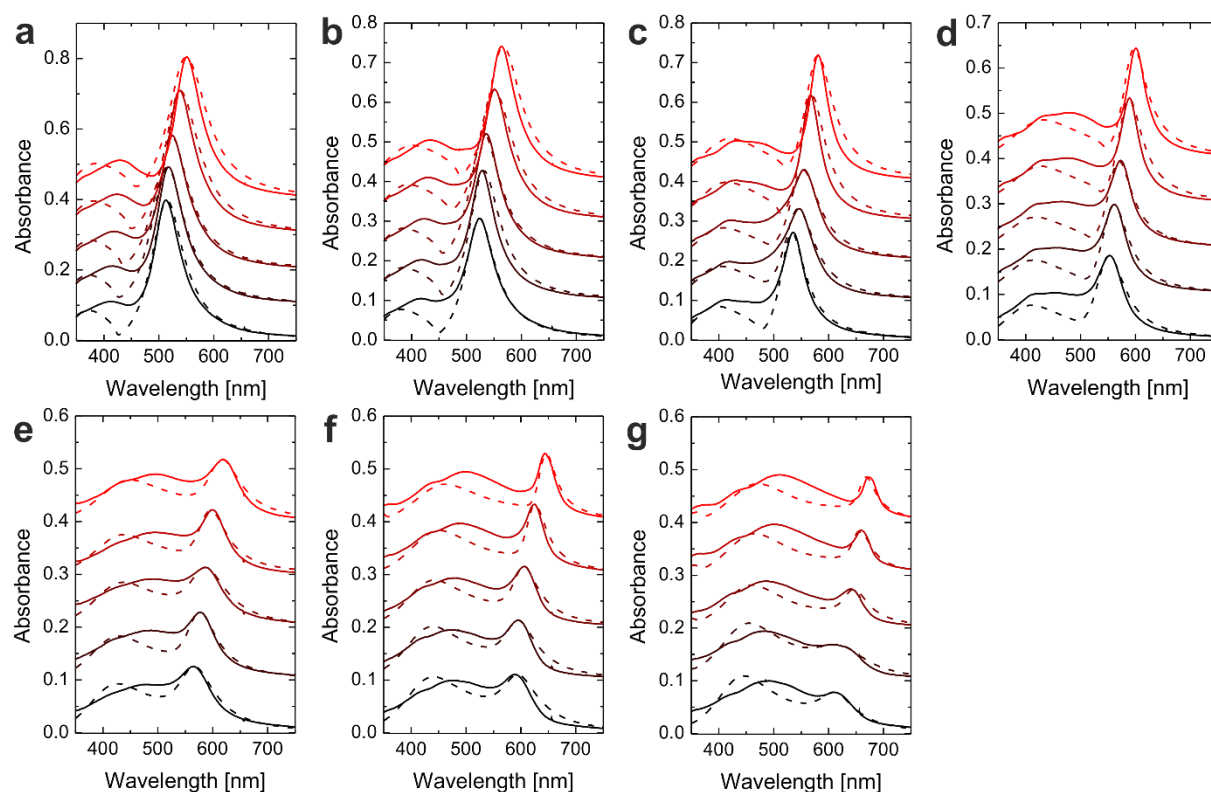


Figure S4. Influence of solvent refractive index and lattice spacing on SLR peak position. Evolution of the absorbance spectra of PNIPAM-coated NC arrays with $d_{c-c} = 356$ nm (a), $d_{c-c} = 374$ nm (b), $d_{c-c} = 407$ nm (c), $d_{c-c} = 419$ nm (d), $d_{c-c} = 451$ nm (e), $d_{c-c} = 474$ nm (f), and $d_{c-c} = 506$ nm (g) immersed in different solvents, from bottom to top: methanol ($n = 1.33$, black trace), ethanol ($n = 1.36$), butanol ($n = 1.40$), chloroform ($n = 1.45$) and toluene ($n = 1.50$). Solid lines are experimental results and dashed lines correspond to the respective fit results from theoretical coupled dipole approximation (CDA) computations. The spectra have offsets in steps of 0.1.

With increasing d_{c-c} , a redshift of the SLR is observed for a given refractive index. For larger values of d_{c-c} mode coupling becomes weaker and a significant contribution of the LSPR can

be seen at lower wavelength. All spectra are well-described by theoretical spectra obtained from coupled dipole approximation (CDA) calculations (dashed lines).

Figure S5 shows the heating and cooling curve of the swelling sample with the larger spacing of $d_{c-c} = 488$ nm. The temperature was increased/decreased in 5 °C steps from 10 to 55 °C and the SLR positions was recorded. The peak positions of the heating and the cooling curve are almost identical proofing that no hysteresis of the polymer film occurs during the temperature cycle.

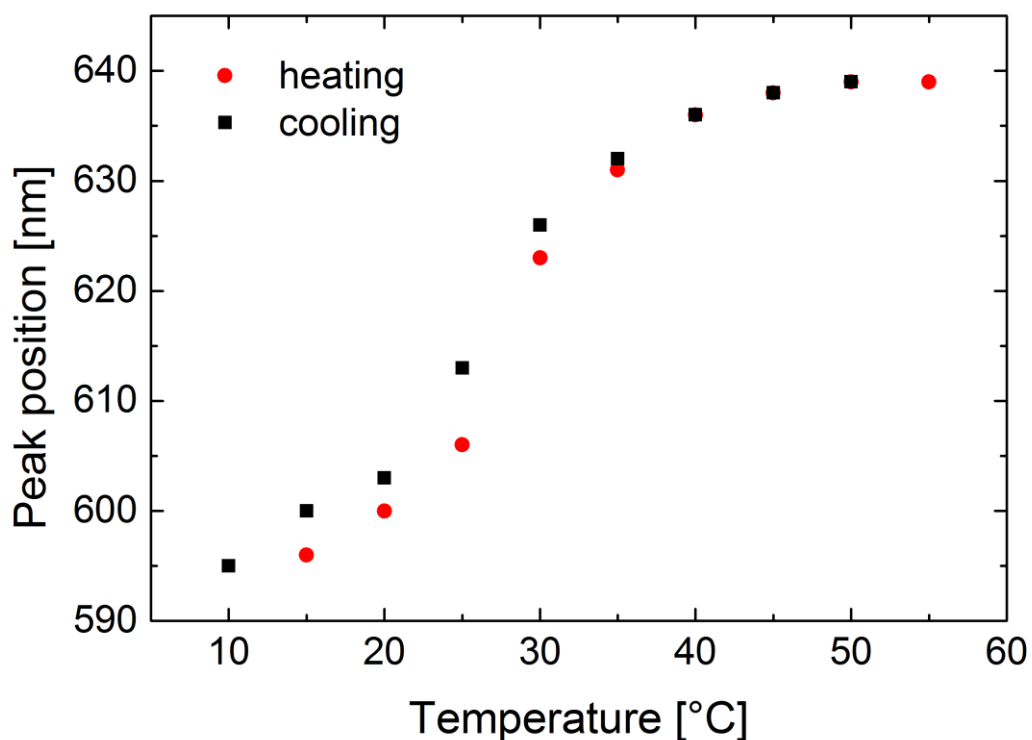


Figure S5: SLR positions measured in a heating (red circles) and a cooling cycle (black squares) for the sample with $d_{c-c} = 488$ nm. The SLR positions overlap almost perfectly and no hysteresis is observed.

In addition to further demonstrate the reversibility of the swelling and deswelling process a larger cycling number was performed with a sample of $d_{c-c} = 495 \pm 40$ nm. In order to increase the cycling number in a reasonable time frame the sample was cooled and heated by placing the cuvette into an ice bath or a water bath at 65 °C, respectively. Since the sample holder in the UVvis device was not temperature controlled the real temperature at which the measurements were performed was slightly increased and decreased, respectively, compared to the heating bathes. Nevertheless 20 cycles were performed using this method and a highly reproducible SLR-shift was demonstrated as depicted in Figure S6. The SLR in the swollen state occurred at 609.2 ± 1.2 nm and the SLR in the collapsed state at 648.5 ± 0.7 nm. Slight

variations mostly likely occur from temperature discrepancies and minimally changing sampling positions and inhomogeneities.

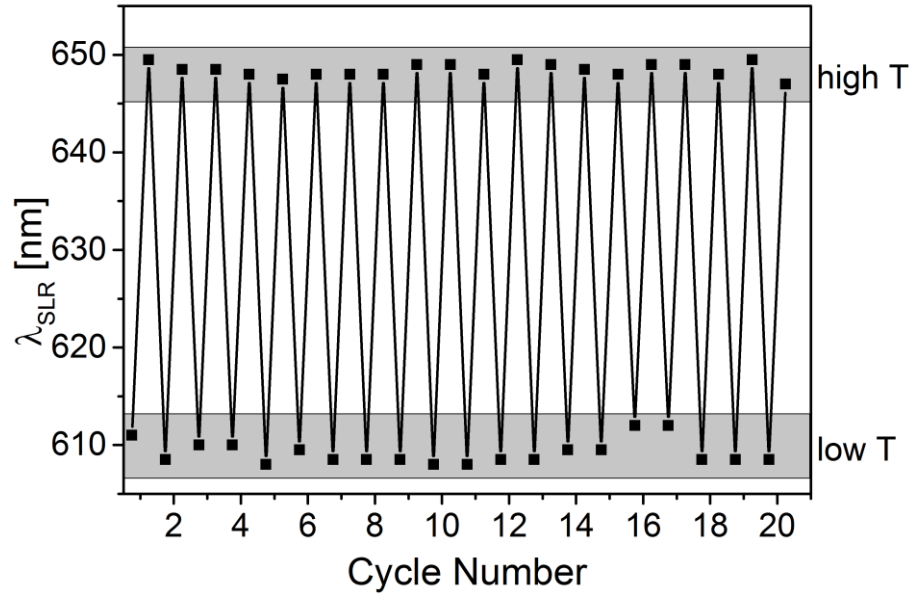


Figure S6: Extended reversibility study in water on SLR tuning with temperature of a device with $d_{c-c} = 495$ nm.

FDTD Simulations

The optical response in transmission and reflection was simulated using a commercial software from Lumerical Solutions, Inc. (FDTD Solutions, Version 8.11.422). We used a hexagonal nanoparticle array with periodic boundary condition (BC) in layer direction and perfectly matched layer (PML) BC in beam direction with a linear polarized plane wave source. Particle diameters, periodicity, multilayer materials and thickness were obtained from the experiment. In beam direction, the FDTD simulation total length was chosen to be $4\ \mu\text{m}$ with transmission monitors located at both ends. The simulation setup was placed in the center of the FDTD simulations and the plane wave source was injected starting from the glass layer. For a broadband source simulation ($\lambda = 300 - 1000$ nm), the FDTD software approximates the refractive index of the materials by a polynomial function. All optical constants were approximated with a RMS error below 0.21. An isotropic mesh overwrite region was used according to the specific periodicity and particle diameter (mesh always 2 nm). All simulations reached the auto shut-off level of 10^{-5} before reaching 1000 fs simulation time. To determine the electric field distribution and surface charge densities, we simulated the model at the plasmonic mode frequency at a pulse length of ~ 20 fs (optimized for long pulse length).

To determine the refractive index of the glass substrate and PNIPAM layer we used M2000 spectroscopic ellipsometer from J.A. Woollam Co. in the wavelength range from 245 nm to

1600 nm (D2 and QTH lamps). Ellipsometric data from all samples were acquired at five different angles of incidence in steps of 5° . To determine the refractive index of all materials we used a general oscillator layer model within the CompleteEASE (Version 5.07) software. All modelling approximations were physically reasonable (parametrization to fulfill Kramers–Kronig relations) and showed a mean square error (MSE) below five.

Coupled dipole approximation (CDA) simulations

While the single nanoparticle dipole response was calculated with experimental parameters using Mie theory,⁶ the extinction spectra of the plasmonic arrays were simulated using the coupled dipole approximation (CDA).⁷ The CDA provides an accurate model of well-spaced arrays of plasmonic nanoparticles⁸ by approximating the NPs as point dipoles and constructing a linear response matrix. In the limit of a perfect, infinite lattice, this leads to a semi-analytic expression for the coupled dipole polarization response. This polarizability can be used to calculate the extinction spectrum of the idealized NP array. Here we use the CDA formulas presented by Draine^{7a} and Schatz^{7c} modified to include an exponential decay in the scattered dipole-coupling fields, as described in a previous work.⁴

Computation of extinction spectra with the CDA requires significantly less computational resources than other multiparticle scattering methods, such as finite-difference time-domain (FDTD), allowing a large survey of experimental parameters to fit the measured extinction spectra. Here, we used the experimentally determined values of the plasmonic core diameters and inter-particle distances (d_{c-c}).

Then, we computed the CDA spectra of silver nanoparticles embedded in a homogeneous medium with refractive index n_{med} ranging over 1.30 – 1.55 with 21 values, using Mie theory to calculate the single-particle polarizability.⁹ Additionally, we surveyed the scattered dipole-coupling field decay constants α over the range 0.074 to 2.00 per lattice spacing with 20 values. In this range, the decay constant has little effect on the SLR peak position, instead primarily determining the peak width and shape. Therefore, we fit the CDA spectra to the solvent experiment first by peak position to determine the effective refractive index of the NP array medium. The width provided a secondary fit parameter, resulting in the best fit CDA spectra presented in Fig. 4 in the main manuscript and Fig. S4. The best fit parameters for n_{med} and α are given in Table S1. The fitted refractive indexes show a clear correlation with the solvent refractive index. From this we can conclude that the PNIPAM layer is fully infiltrated with solvent. This approach was also adapted to the temperature-dependent experimental spectra, as shown in Fig. 5 (main manuscript), resulting in effective refractive indexes ranging from 1.33

– 1.35 (cold) to 1.40 – 1.45 (hot), consistent with the refractive indexes of swollen and collapsed PNIPAM, respectively.

Table S1. Best fit parameters of the CDA computations to the spectra in solvents, as indexed by sample inter-particle spacing d_{c-c} (down) and solvent (across). Each cell contains (n_{med} , α), where n_{med} is the effective refractive index and α is the scattered field (dipole-coupling) decay constant per lattice spacing d_{c-c} .

d_{c-c} (nm)	Methanol	Ethanol	Butanol	Chloroform	Toluene
356	1.375 0.074	1.375 0.125	1.40 0.074	1.45 0.074	1.475 0.21
374	1.375 0.105	1.40 0.074	1.40 0.105	1.45 0.177	1.50 0.074
407	1.35 0.149	1.375 0.354	1.40 0.297	1.45 0.074	1.475 0.177
419	1.375 0.354	1.40 0.25	1.425 0.177	1.475 0.149	1.50 0.125
451	1.35 0.841	1.375 0.595	1.40 0.841	1.425 0.5	1.475 0.595
474	1.375 0.841	1.375 0.707	1.40 0.5	1.45 0.297	1.50 0.21
506	1.35 0.841	1.375 1.189	1.425 0.5	1.45 0.354	1.475 0.296

Effect of domain size on SLR optical properties using the CDA model. The samples investigated here are composed of large, but finite-size crystalline domains of plasmonic nanoparticles. Using the CDA model described above, we investigated the effect of domain size. The hexagonal lattices investigated have $d_{c-c} = 497$ nm, an effective refractive index of 1.42, and arrays containing 1, 7, 19, and 9271 nanoparticles, representing an uncouple response, very small domains, and a semi-infinite case. The results are shown in Fig. S7. This brief study demonstrates that an SLR can be supported by only a few nanoparticles (19 plasmonic cores, in green) and is already qualitatively similar to an effectively infinite lattice (red). The positions of the (10) and (11) lattice diffraction modes are also noted.

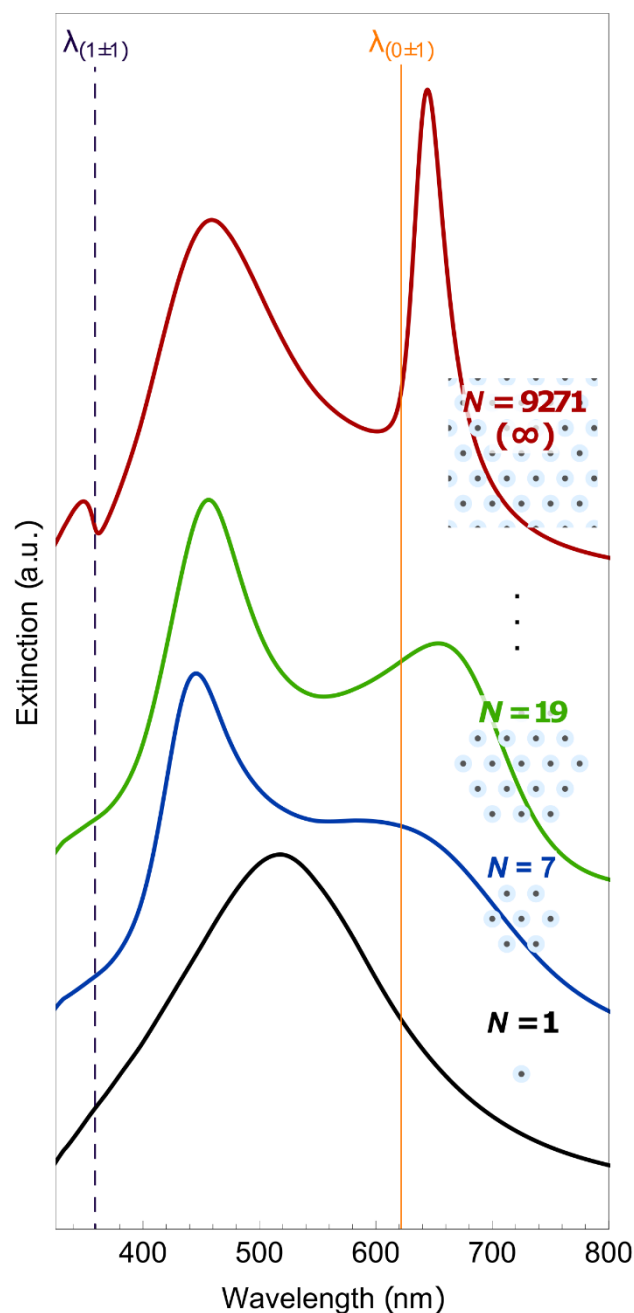


Figure S7. Using the CDA model, the role of domain size on the onset of an SLR is investigated for a lattice with a variable number of plasmonic cores. Here the lattice spacing is 497 nm and the surrounding refractive index is 1.42. As can be seen, the first indications of an SLR emerge with only one ring of nanoparticles (blue trace), and it clearly visible, albeit with a broad linewidth, with two rings of nanoparticles (green trace). These cases are compared to the single nanoparticle spectrum (black trace) and the effectively infinite case (red). The lattice diffraction modes are highlighted in orange at 610 nm for the (10) mode and gray (dashed) at 360 nm for the (11) mode.

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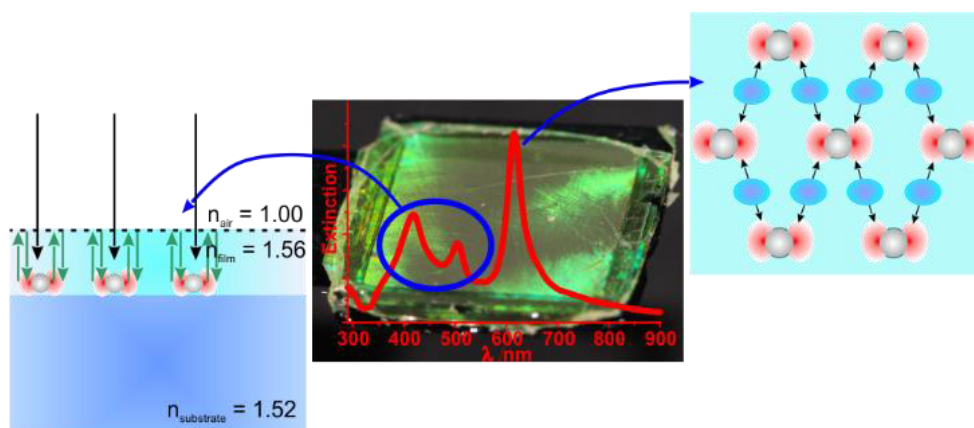
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6 In-Plane Surface Lattice and Higher Order Resonances in Self-Assembled Plasmonic Monolayers: From Substrate-Supported to Free-Standing Thin Films

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Keywords: surface plasmon resonance, higher order mode coupling, plasmonics, nanoparticle arrays, self-assembly, free-standing films



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Abstract

Periodic arrays of plasmonic nanostructures are able to strongly confine light at the nanometer scale because of surface lattice resonances. These resonances are the result of electromagnetic coupling between single-particle localized surface plasmon resonances and Bragg resonances of the periodic lattice. Here, we investigate the effect of a finite size refractive index environment on the formation of surface lattice resonances by increasing the thickness of a polymer coating in nanometer-scale increments. Wet-chemically synthesized, spherical silver and gold nanoparticles with soft hydrogel shells are self-assembled into macroscopic, hexagonally ordered arrays on glass substrates using an interface-assisted approach. The resulting periodic plasmonic monolayers are subsequently coated by a polymer coating matching closely the refractive index of the glass support. The optical response of the coated plasmonic arrays is studied using far-field extinction spectroscopy and supported by numerical simulations. We show the formation of surface lattice resonances as well as higher order resonances in finite thickness polymer coatings. The resonance positions are determined by the inter-particle spacing as well as the plasmonic material. Additionally we demonstrate that a coating thickness of 450 nm is sufficient to support strong in-plane surface lattice resonances. This enables us to prepare macroscopic, free-standing polymer films with embedded plasmonic nanoparticle arrays, which feature strong surface lattice resonances.

Introduction

Two-dimensional periodic superstructures of plasmonic nanoparticles have recently gained attention in different fields of research because of their fascinating optical properties and their potential applications in nanooptics, where the controlled confinement of optical fields in space and time plays a major role.¹⁻⁵ Single gold or silver nanoparticles exhibit localized surface plasmon resonances (LSPRs) in the visible wavelength range. Such LSPRs originate from coherent oscillations of the free electrons of the nanoparticles excited by an incoming electromagnetic wave.⁶⁻⁸ The resonance position and strength can be tailored by the size, shape and material of the plasmonic nanostructure.⁹⁻¹⁰ Upon excitation, the electromagnetic field close to the nanoparticle surface is strongly enhanced.¹¹ In periodic arrays of plasmonic nanostructures with interparticle spacings comparable to the wavelength of visible light, far-field electromagnetic coupling between the single-particle LSPRs and Bragg resonances can occur, provided that both modes have a sufficient spectral overlap.¹²⁻¹⁸ This plasmonic/diffractive coupling is characterized as surface lattice resonances (SLRs) with peak positions determined by the lattice period,^{13, 19-20} lattice geometry,²¹⁻²² refractive index (RI) environment^{19-20, 23} and particle material, size and shape.^{13, 17, 24} Precisely, the SLR wavelength

is proportional to the inverse of the polarizability α of the individual particles²⁵⁻²⁶ and is located at the intersection of the real part of the array factor S , which depends on particle separation and arrangement, with α when plotted against the wavelength.²¹ The in phase excitation of the individual particle plasmon oscillations resulting from the formation of standing waves in the lattice plane requires constructive interference. This constructive interference only appears at the longer wavelength side of the diffraction modes.²⁷ Furthermore, SLRs are typically observed with narrow bandwidths, that is, significantly longer plasmon lifetimes than the relatively broad single particle LSPRs.²⁸⁻²⁹ While the LSPR lifetime suffers from radiative losses and metallic intra- and interband absorption losses,³⁰ SLRs benefit from coupling to high quality diffractive modes (few nm width). Thus, SLRs combine the high field enhancements from plasmonic nanostructures with long-lived lifetimes from the photonic lattice.²⁷ Here, the scattered light of a particle is in phase with the plasmon resonance induced in its neighbouring particle. Consequently, the scattered fields can counteract the damping of single nanoparticles.³ As a result, SLRs are an exciting area of active research into using plasmon resonances for coherent optical processes, such as lasing,³¹⁻³⁴ energy transfer³⁵⁻³⁶ and sensing.³⁷⁻⁴⁰

In previous works, it was found that a homogeneous RI environment surrounding the plasmonic array is vital for the formation of SLRs.^{13-14, 19, 41-42} In contrast, for plasmonic particle lattices that are placed close to a material interface with a significant RI mismatch, for example, a glass/air interface, electromagnetic coupling to diffractive modes is weak or absent. In the latter case, the lattices exhibit spectral resonances more similar to the individual, uncoupled LSPRs. To date, the transition from nearly uncoupled LSPRs to the strongly coupled collective SLRs in the effectively infinite medium has not been investigated experimentally and remains poorly understood. Furthermore, from an application point of view, employing SLRs in real applications is hindered by the semi-infinite oil coatings or polymer-based binding layers used so far in combination with cover glasses, which are incompatible with the device miniaturization as an inherent goal of nanooptics.

Here, we systematically study the influence of an inhomogeneous RI environment on electromagnetic coupling in hexagonally ordered particle arrays with inter-particle spacings in the visible wavelength range. We do this by first preparing particle arrays on glass substrates. Here, the highly inhomogeneous RI environment with glass and air as the superstrate prevents electromagnetic coupling in the particle lattice.

Then, we begin to homogenize the RI by the stepwise application of a polymer coating with an RI that closely matches that of the glass substrate. We vary the thickness of this coating, d_{film} ,

over hundreds of nm using small, nanometerscale increments. Thereby, the distance between the particle array and the polymer/air interface is systematically increased. This allows us to closely monitor the appearance and spectral position of in-plane SLRs and higher order resonances at shorter wavelengths that depend on the distance between the scattering plane, that is, the particle lattice plane, and the polymer/air interface.

In order to better understand the physical origin of the higher order resonances that appear for finite thickness RI coatings, we take a two-fold approach: first, we experimentally study the optical response of lattices produced from two different types of plasmonic particles, namely, silver and gold. These possess LSPRs which are approximately 80 nm apart from each other, allowing us to investigate the influence of the LSPR position on far-field coupling. Second, we compare the experimental spectra to optical simulations using the finite difference time domain (FDTD) method.^{34, 42-44} As a result, we develop a robust physical intuition for SLRs and higher order resonances in a finite-size homogeneous RI medium. We also show that polymer coatings of 450 nm thickness are sufficient to obtain pronounced SLRs and thereby device miniaturization in z-direction becomes possible. This ultimately allows us to prepare free-standing films with embedded plasmonic nanoparticle arrays and total thicknesses in the range of one micron that show strong SLRs.

Experimental Details

Chemicals

Silver nitrate (99.999 %, Sigma), ascorbic acid (p.a., Roth), acetonitrile (HPLC grade, Fisher Chemicals), ethanol (p.a., Honeywell), 1,4-dioxane (p.a., Fisher Chemicals), Norland Optical Adhesives (NOA81, Norland Products), Hellmanex III (Hellma GmbH), zinc acetate dihydrate (99.999 %, Sigma), 2-aminoethanol (for synthesis, Roth), 2-methoxyethanol (for synthesis, Roth) and hydrochloric acid (1 M, p.a., VWR chemicals) were used as perceived. Purified water (MQ water) from a Milli-Q system (Millipore) with a final resistivity of 18.2 MΩcm was used for all synthesis, purification and assembly steps.

Particle Synthesis

Core/shell particles with gold or silver nanoparticle cores and cross-linked hydrogel shells were synthesized in three steps, which are all easy to scale up in order to produce large quantities. First, spherical gold nanoparticles were synthesized according to the well-established Turkevich method.⁴⁵ In the second step the gold particles were encapsulated by a poly-(*N*-isopropylacrylamide) (PNIPAM) hydrogel shell after gold surface functionalization following a method reported by Karg *et al.*⁴⁶ This resulted in core/shell particles with spherical cores of approximately 14 nm in diameter and hydrogel shells with an overall hydrodynamic diameter

of 336 nm (20°C, swollen state). In a third step the cores of these core/shell particles were either overgrown with gold or with silver to yield overall core sizes of approximately 100 nm in diameter. In the following, we refer to these core/shell particles as Au-PNIPAM (100 nm gold cores) and Ag-PNIPAM (100 nm gold/silver core/shell cores). Overgrowth with gold was done following the protocol from Honold *et al.*,⁴⁷ while the overgrowth with silver was performed as described in the following: 2.65 mL of MQ water and 500 μ L of acetonitrile were mixed in a roundbottom flask that is placed in an ice bath. Under continuous stirring with a magnetic stirring bar, 79 μ L of an aqueous 2 wt.-% dispersion of the gold/hydrogel core/shell particles with 14 nm gold cores were slowly added. After that 2 mL of a freshly prepared, ice cold, aqueous ascorbic acid solution (49 mM) and 5.05 mL of a silver nitrate solution (15 mM) were added rapidly. The reaction was allowed to continue for 30 minutes under cooling and stirring. After warming to room temperature, the dispersion was purified using centrifugation (3 times, 2400 rcf for 20 min) and redispersion in water, then ethanol and at the end in water again.

Monolayer Preparation

The preparation of the hexagonally ordered nanoparticle arrays was conducted by self-assembly at the air/water interface and subsequent transfer onto glass substrates following a previously published protocol.¹⁹ The resulting substrate-supported colloidal monolayers were then coated with a RI matching polymer, NOA 81 (NOA), by spin-coating a stock solution of NOA in 1,4-dioxane (16.4 mg/mL). The spin-coating process was conducted at 2000 rpm for 90 seconds. After 30 seconds of spinning, a UV lamp ($\lambda_{em} = 366$ nm), which was placed directly above the spinning sample, was turned on in order to initiate UV curing of the NOA polymer. Like this a first polymeric film of approximately 42 nm thickness was obtained. For larger film thicknesses, the latter process was repeated up to a maximum total thickness of approximately 1750 nm. For each obtained film thickness, UV-vis absorbance measurements were performed.

Preparation of a Free-Standing Film

In order to prepare free-standing polymer films that encapsulate our plasmonic colloidal monolayers, we employed glass substrates with a sacrificial ZnO layer that was prepared using a sol-gel method.⁴⁸⁻⁴⁹ Initially, glass slides were cleaned by sonication for 15 min in an aqueous Hellmanex solution (2 vol%). After that the glass substrates were rinsed with MQ water, further sonicated in ethanol for 15 min and finally dried with compressed N₂. The substrates were treated with O₂-plasma for 15 s directly before application of the ZnO layer. The ZnO film was prepared by spin-coating a zinc acetate solution (110 mg zinc acetate dihydrate in 32 μ L of 2-aminoethanol and 1 mL of 2-methoxyethanol) at 2000 rpm for 90 s and subsequent baking at 150 °C for 5 min. Then, this step was repeated in order to increase the ZnO layer thickness.

Next, an approximately 450 nm thick NOA film (exact thickness from AFM: 449 ± 34 nm) was prepared on top by spin-coating a NOA solution (140 mg of NOA in 1 mL of 1,4-dioxane) at 2000 rpm for 90 s. After 45 s of spinning, a UV lamp ($\lambda_{em} = 366$ nm), which was placed directly above the spinning sample, was turned on in order to initiate UV curing of the NOA polymer. After the spin-coating process had finished, curing was continued for 1 min. For the monolayer deposition, the surface of the NOA film on the glass/ZnO substrate was treated with O₂-plasma for 1 min before the particle monolayer was collected from the air/water interface on top of the NOA film. Then, a 450 nm thick NOA top coating was applied by repeating the spin-coating and curing process. For the detachment of the NOA/Ag-PNIPAM monolayer/NOA film, the ZnO sacrificial layer was dissolved by immersion of the whole sample in an aqueous HCl bath (pH 1) for 12 h. With the help of tweezers the film was then carefully lifted to the air/water interface and collected onto a 3D-printed PET frame. The film was dried under ambient conditions. The PET frame was printed from 1.75 mm diameter PETG filament (Renkforce) using a Prusa i3 MK3 3D printer with standard settings for generic PET filament using 20% infill and 0.1 mm resolution. The square shaped frame had overall dimensions of 1 cm x 1 cm (1 mm thickness) with an inner square shaped hole of 0.8 cm x 0.8 cm and was attached to a rectangular handle for easy handling (see e.g. Figure 6e).

FDTD Simulations

The optical response in transmission and reflection was theoretically calculated using the FDTD approach with commercial software from Lumerical Solutions, Inc. (FDTD Solutions, Version 8.18.1332). We used a hexagonal nanoparticle array with periodic boundary conditions (BCs) in x,y -direction (layer direction) and perfectly matched layer BC in z -direction (beam direction) with a linear polarized plane wave source injected along the z -axis. Particle diameters, periodicities, multilayer materials, and film thicknesses were used as obtained from the experiment. In beam direction, the FDTD simulation total length was chosen to be 3.5 μ m with transmission monitors located at both ends. The simulation setup was placed in the center of the FDTD simulation and the plane wave source was injected starting from the glass layer. For the broadband source simulation ($\lambda = 290 - 910$ nm), the FDTD software approximates the refractive index (RI) of silver⁵⁰ and gold⁵¹ to literature values by a polynomial function. The glass substrate was simulated with a RI of 1.52, the dry and collapsed PNIPAM shell directly surrounding the plasmonic particles with a RI of 1.49, a slightly smaller value than reported by Brasse *et al.*⁵² (1.50) to account for some residual water in our collapsed PNIPAM shells, the immersion oil with a RI of 1.54 and the air background with a RI of 1. We only expect a small wavelength dependence of the RIs for the aforementioned materials in the investigated spectral

range and thus used constant values of RI for these. For the NOA polymer film a constant RI of $1.56 + 0.01i$ was applied. The real part was determined by ellipsometry and the small imaginary part accounts for small absorptive losses in the polymer coating. An isotropic mesh overwrite region was used according to the specific periodicity and particle diameter (mesh always 3.5 nm). All simulations reached the auto shut-off level of 10^{-5} before reaching 1000 fs simulation time.

Atomic force microscopy

Topographic AFM images ($10 \times 10 \mu\text{m}^2$) were recorded with a Nanowizard 4 (JPK Instruments) in intermittent contact mode against air. OTESPA-R3 AFM probes (Bruker) were employed for image recording. The cantilevers possess a resonance frequency of approximately 300 kHz and a spring constant of approximately 26 N/m. The tip geometry was a visible apex with a nominal tip radius of 7 nm.

Extinction Measurements

Extinction measurements were performed with an Agilent 8453 UV-vis spectrometer equipped with a temperature-controlled sample holder. Spectra were recorded in the wavelength range of 250 - 1019 nm in transmission geometry. Spectra of particle dispersions were recorded in $1 \times 1 \text{ cm}^2$ quartz glass cuvettes closed with Teflon stoppers. The colloidal monolayer samples were positioned upright in the light path using a solid sample holder. All spectra were background and substrate corrected and converted into absorbance spectra.

Results and Discussion

Colloidal Building Blocks for the Preparation of Plasmonic Nanostructures

Core/shell colloids with plasmonic metal nanoparticle cores and soft hydrogel shells composed of cross-linked PNIPAM are the building blocks for the plasmonic monolayers studied in this work. The core/shell particles were prepared by seeded precipitation polymerization and successive overgrowth of the metal cores by either gold (Au-PNIPAM) or silver (Ag-PNIPAM) to the desired core size as described in the Experimental Details section. Figure 1a shows a representative transmission electron microscopy (TEM) image of particles containing silver nanoparticle cores.

The core/shell morphology is clearly visible because of the strong electron contrast between the metal cores and the surrounding hydrogel shell. From TEM, we can determine the mean diameter of the silver nanoparticle cores $d_{\text{Ag}} = 101 \pm 10 \text{ nm}$. A TEM image of the Au-PNIPAM core/shell particles with a mean core diameter of $d_{\text{Au}} = 100 \pm 7 \text{ nm}$ can be found in the Supporting Information in Figure S1a. Because of the removal of water from the hydrogel shells prior to TEM imaging and the high vacuum conditions during the TEM investigation, the

hydrogel shells are imaged in their dried and almost fully collapsed state. In contrast, the shells will be swollen by the solvent in aqueous dispersion leading to significantly larger overall particle dimensions. The overall hydrodynamic diameter in dilute aqueous dispersion was determined by dynamic light scattering as $d_h(\text{core/shell}) = 336 \text{ nm}$ (20 °C, the swollen state of the PNIPAM shell) for both core/shell systems.

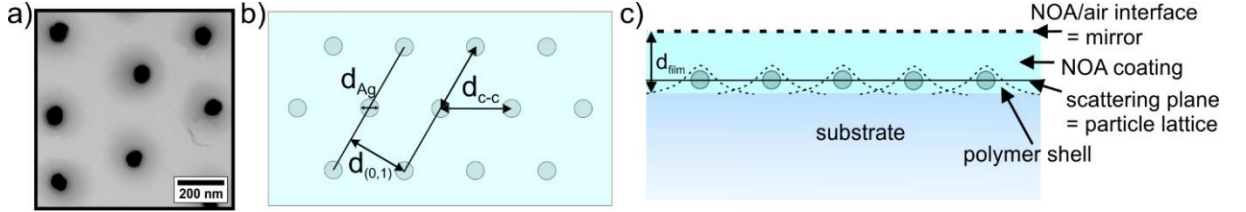


Figure 1. Colloidal building blocks and sample layout. (a) Bright-field TEM image of Ag-PNIPAM core/shell colloids. (b) Top-view sketch of a hexagonally ordered monolayer of plasmonic particles with diameter d_{Ag} and nearest neighbor center-to-center distance $d_{\text{c-c}}$. $d_{(0,1)}$ is the interplanar spacing as an example for the $\{0,1\}$ group. The PNIPAM shells were omitted for the sake of clarity. (c) Side-view sketch of polymer-embedded particle monolayer on glass (substrate, in blue).

When these core/shell particles arrange into densely packed monolayers, the hydrogel shells control the center-to-center nearest neighbor distance $d_{\text{c-c}}$, leading to non-close packed arrangements of the plasmonic metal cores as schematically illustrated in Figure 1b. The sketch shows the top-view illustration of a hexagonally ordered nanoparticle array with d_{Ag} , $d_{\text{c-c}}$ and the interplanar spacing $d_{(0,1)}$. For the sake of clarity the hydrogel shells were omitted in this illustration. In this work, all the monolayer samples were prepared on glass substrates (1 mm thickness). This was done in a two-step process as previously reported by us:^{41, 47} in the first step, hexagonally ordered, freely floating monolayers of the core/shell colloids were prepared by self-assembly at the air/water interface. In the second step, the freely floating monolayers were transferred onto the glass substrates. To enable strong resonance coupling in these samples, we embedded the substrate supported monolayers into polymer films (NOA) of various thicknesses d_{film} as achieved via spin-coating. Figure 1c shows a side-view sketch of such a nanoparticle array sandwiched between the glass support (substrate, blue color) and the NOA film (coating, cyan color). In this illustration, the collapsed hydrogel shells covering the plasmonic monolayer are also schematically depicted. The core/shell structure and the collapse of the shell lead to a fried-egg like morphology of the particles on the substrate. This effect can also be seen in the AFM height image in Figure S2a and the cross-section in (c), where a line profile through the center of a particle in the array is shown. The average maximum particle height is $131 \pm 9 \text{ nm}$ and thus larger than the size of the encapsulated core ($d_{\text{Ag}} = 101 \pm 10 \text{ nm}$) because of the collapsed shell material below and above the metal core (approximately 15 nm

each). Thus we can assume that the plasmonic cores are not in direct contact with the glass substrate. Taking into account this gap of approximately 15 nm between the metal cores and the glass substrate as well as the core diameter ($d_{\text{Ag}} \approx d_{\text{Au}} \approx 100$ nm), we can calculate the position of the particle centers (scattering plane) within our samples to 65 nm above the glass substrate (15 nm gap + $d_{\text{Ag/Au}}/2$).

Optical properties of colloids in dispersion and colloidal monolayers

Figure 2 summarizes photographs, microscopy images as well as UV-vis absorbance spectra recorded at different stages of the preparation of our plasmonic nanostructures. Figure 2a shows digital photographs of the Ag-PNIPAM (left) and Au-PNIPAM (right) core/shell building blocks in dilute aqueous dispersions. The colloids are well dispersed and colloidally stable, and the dispersions possess the characteristic gray and orange-red color for silver and gold nanoparticles of 100 nm diameter. The pronounced turbidity of the samples is on the one hand related to the already significant scattering contribution of the rather large metal cores. On the other hand, the PNIPAM shells efficiently scatter incoming light. Both particle dispersions feature broad dipolar LSPRs as depicted in the absorbance spectra in Figure 2b with resonance positions of $\lambda_{\text{LSPR}}(\text{Ag-PNIPAM}) = 500.5$ nm and $\lambda_{\text{LSPR}}(\text{Au-PNIPAM}) = 578.5$ nm, respectively. Additionally, the spectrum of Ag-PNIPAM shows a weak shoulder at 413.5 nm that can be assigned to a quadrupolar LSPR. Because of the slightly higher polydispersity of the silver cores in the Ag-PNIPAM sample and the additional quadrupolar contribution, the apparent width of the LSPR peak is slightly larger for Ag-PNIPAM than for Au-PNIPAM. Figure 2c shows a representative AFM image of a hexagonally ordered monolayer prepared with the Ag-PNIPAM colloids on glass. A corresponding AFM image of a monolayer prepared from Au-PNIPAM colloids is shown in the Supporting Information (Figure S1b). The lattices are characterized by $d_{\text{c-c}} = 503 \pm 27$ nm ($d_{(0,1)} = 436$ nm) for Ag-PNIPAM and $d_{\text{c-c}} = 510 \pm 24$ nm ($d_{(0,1)} = 442$ nm) for Au-PNIPAM. As shown in the spectra in Figure 2d, both monolayers feature the characteristic LSPRs of the respective colloids with $\lambda_{\text{LSPR}} = 538.5$ nm for the Ag-PNIPAM and $\lambda_{\text{LSPR}} = 588$ nm for the Au-PNIPAM monolayer. Both values are slightly red-shifted with respect to the LSPRs measured from dilute dispersion. This is related to the slightly RI environment because of the underlying glass substrate ($\text{RI}_{\text{glass}} = 1.52$) and the collapsed PNIPAM hydrogel shell ($\text{RI}_{\text{shell}} = 1.49$).⁵³

Because the arrays are placed in an inhomogeneous RI environment with the glass substrate on the one side and air ($\text{RI}_{\text{air}} = 1$) on the other side, coupling between the LSPRs and diffractive modes does not take place.^{13-14, 19, 41-42} Instead, the LSPRs remain rather broad: the full width at half maximums are as follows: $\text{fwhm}(\text{Ag-PNIPAM}) = 166$ nm and $\text{fwhm}(\text{Au-PNIPAM}) = 109$

nm. A straightforward way to homogenize the RI environment is to apply immersion oil ($RI_{oil} = 1.54$) on top of the colloidal monolayer (Figure 1e). Now the absorbance spectra of the two monolayers (Figure 2f) look significantly different as compared to the monolayers on glass against air. Sharp SLRs form as the consequence of plasmonic/diffractive coupling with the $(1,0)/(0,\pm 1)$ Bragg modes (i.e. $\{1,0\}$) of the lattice with center wavelengths of $\lambda_{SLR} = 682$ nm for the Ag-PNIPAM and $\lambda_{SLR} = 697$ nm for the Au-PNIPAM monolayer. Furthermore, the samples feature broad resonance peaks at lower wavelengths corresponding to a plasmonic contribution of the individual particles.^{13, 22, 42} To benefit from the narrow SLRs in potential applications, for example, in sensing or lasing, the application of immersion oil is impractical. Thus, a coating with a thin and stable layer that homogenizes the RI environment is much more desirable. Therefore, we prepared samples where the colloidal monolayers were coated with a polymer film (NOA 81, $RI_{NOA} = 1.56$) by spin-coating (see Figure 2g). Samples with an average film thickness of $d_{film} = 224$ nm feature SLRs at $\lambda_{SLR} = 671$ nm for the Ag-PNIPAM and at $\lambda_{SLR} = 684.5$ nm for the Au-PNIPAM monolayer (Figure 2h). In addition, the quality factor $QF = \lambda_{Resonance}/fwhm_{Resonance}$ of the resonances is significantly increased from 3.2 (particle monolayer on glass) to 25.7 (particle monolayer with NOA coating) for Ag-PNIPAM and from 5.4 to 19.8 for Au-PNIPAM, respectively. For hexagonally ordered particle arrays, the spectral position of the Bragg diffraction modes can be calculated using eqs 1 and 2. First, the interplanar spacing d is calculated for hexagonal crystal systems in 2D. Therefore, the expression for a 3D hexagonal crystal⁵⁴⁻⁵⁵ is reduced to the 2D case by taking only in-plane terms into account. h and k are the Miller indices and a is the lattice constant. In our case a is equal to d_{c-c} . A short derivation for this 2D diffraction case can be found in the Supporting Information.

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) \quad (1)$$

Then, the diffraction wavelength in transmission geometry at normal incidence can be obtained by multiplication with the RI of the surrounding environment:¹⁴

$$\lambda_{hk} = RI * d \quad (2)$$

We use an average RI of 1.515 (for determination see Figure S6 in the Supporting Information) because of the finite coating that leads to an effectively lower RI than that observed in a completely homogeneous polymer coating. This results in a calculated Bragg mode at 660 nm for $d_{c-c} = 503$ nm and at 665 nm for $d_{c-c} = 510$ nm.

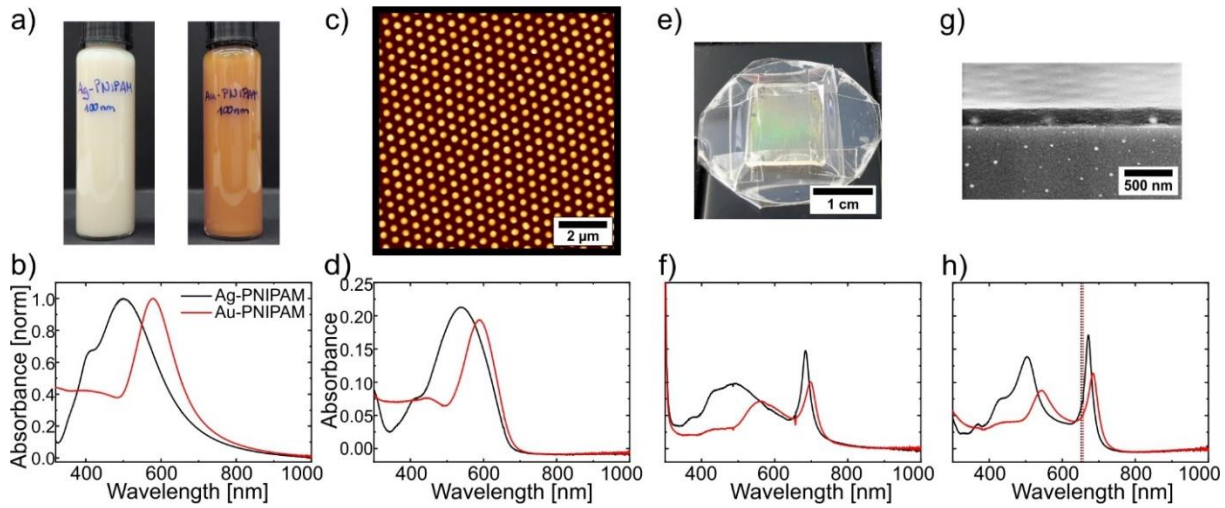


Figure 2. Particles in dispersion and colloidal monolayers. (a) Digital photographs of aqueous Ag-PNIPAM (left) and Au-PNIPAM (right) dispersion. (b) UV-vis absorbance spectra of Ag-PNIPAM (black trace) and Au-PNIPAM (red trace) nanoparticles in aqueous dispersion, normalized to the maximum absorbance at the LSPR peak. (c) AFM image of Ag-PNIPAM particles self-assembled into a monolayer and (d) UV-vis absorbance spectra of hexagonally ordered nanoparticle arrays with $d_{c-c}(\text{Ag-PNIPAM}) = 503$ nm (black) and $d_{c-c}(\text{Au-PNIPAM}) = 510$ nm (red). (e) Digital photograph of the top-coated Ag-PNIPAM sample covered with coverslip and immersion oil and (f) corresponding UV-vis absorbance spectra of Ag-PNIPAM (black) and Au-PNIPAM (red) samples covered with immersion oil. (g) SEM side-view image of the Ag-PNIPAM sample coated with NOA and (h) UV-vis absorbance spectra of the arrays coated with 224 nm NOA. The dotted vertical lines indicate the respective $\{1,0\}$ Bragg resonance wavelengths for the hexagonally ordered Ag-PNIPAM (black) and Au-PNIPAM (red) arrays.

Because of the dependence of the SLR position on the inverse polarizability α of the individual particles^{26, 55} and the array factor S^{21} , as explained in the introduction, the observed SLRs in Figure 2h appear at slightly longer wavelengths than the Bragg resonances (vertical lines) in agreement to the findings in the literature.²⁷ Apart from the sharp SLRs, both samples exhibit a second resonance feature at 503.5 nm for the Ag-PNIPAM and at 543 nm for the Au-PNIPAM array. These shorter wavelength features look qualitatively different from the broad single particle resonance, reported as a residual plasmonic contribution in the literature²² and as observed for our monolayer samples immersed in oil (Figure 2f). In the following section, we will address the properties of these resonance peaks and their dependence on the thickness of the NOA polymer coating.

Optical Properties of Colloidal Monolayers in Dependence of Coating Thickness

To investigate the influence of the NOA coating thickness on the optical response of our plasmonic monolayers, we used the Ag-PNIPAM monolayer with $d_{c-c}(\text{Ag-PNIPAM}) = 503$ nm. Subsequently, we applied NOA coatings on top of the plasmonic monolayer with approximately 42 nm thickness for each coating step. The sketches on the right in Figure 3 visualize the sample

structure at different stages of coating, and selected thickness values are highlighted in between both plots of Figure 3a,b. After each coating step, UV-Vis spectra were recorded in transmission with normal incidence. Figure 3a shows the respective experimental spectra starting with the monolayer on glass without NOA coating (black spectrum) up to a coating thickness of approximately 1750 nm (second blue spectrum from top). In addition, a spectrum recorded after an additional top coating with immersion oil providing an effectively infinite RI environment is shown as the blue spectrum at the top. The spectrum of the monolayer against air (no NOA coating) shows the typical broad LSPR of the Ag-PNIPAM colloids at $\lambda_{\text{LSPR}}(\text{Ag-PNIPAM}) = 538.5 \text{ nm}$ (compare Figure 2d). The spectral region of the LSPR is highlighted as red, vertical lines over the whole height of the graph in Figure 3a. Already after the first coating step with NOA the spectral features change dramatically: a SLR with a reduced fwhm forms at significantly larger wavelengths with respect to the initial LSPR. With increasing coating thickness, the SLR shifts further to the red until a steady SLR position at $\lambda_{\text{SLR}}(\text{Ag-PNIPAM}) = 681 \text{ nm}$ is observed for a NOA thickness of 392 nm up to the final applied coating thickness of 1750 nm and even the oil coated sample. In addition to the SLR, pronounced resonances appear in the lower wavelength region of the LSPR (spectral area in between red lines) and red-shift with increasing NOA thickness. At the same time, the number of these resonances increases with increasing NOA thickness starting with only one resonance for the thinnest to almost ten resonances for the thickest NOA coating. The simulated spectra from FDTD shown in Figure 3b do not only support these observed trends, but also match very well with the experimental spectra. The main difference between the experiment and simulation is the resonance intensities particularly in the lower wavelength region. We assume that this discrepancy is related to the polymer/air interface of the experimental samples. For the simulation, a perfectly flat polymer coating is assumed, while in reality, the spin-coated top-coating is corrugated by the particles (compare side-view SEM image, Figure 1g) and also possesses some surface roughness inherent to the spin-coating process (Figure S2b, RMS of bare NOA film: 0.5 nm/ peak-to-valley roughness: 2.9 nm). This roughness is also responsible for the fact that sharp resonances can be distinguished in the simulated spectra between 350 nm and the $\{1,1\}$ diffraction edge at 392 nm but not in the experiment, where only one broad resonance is detectable.

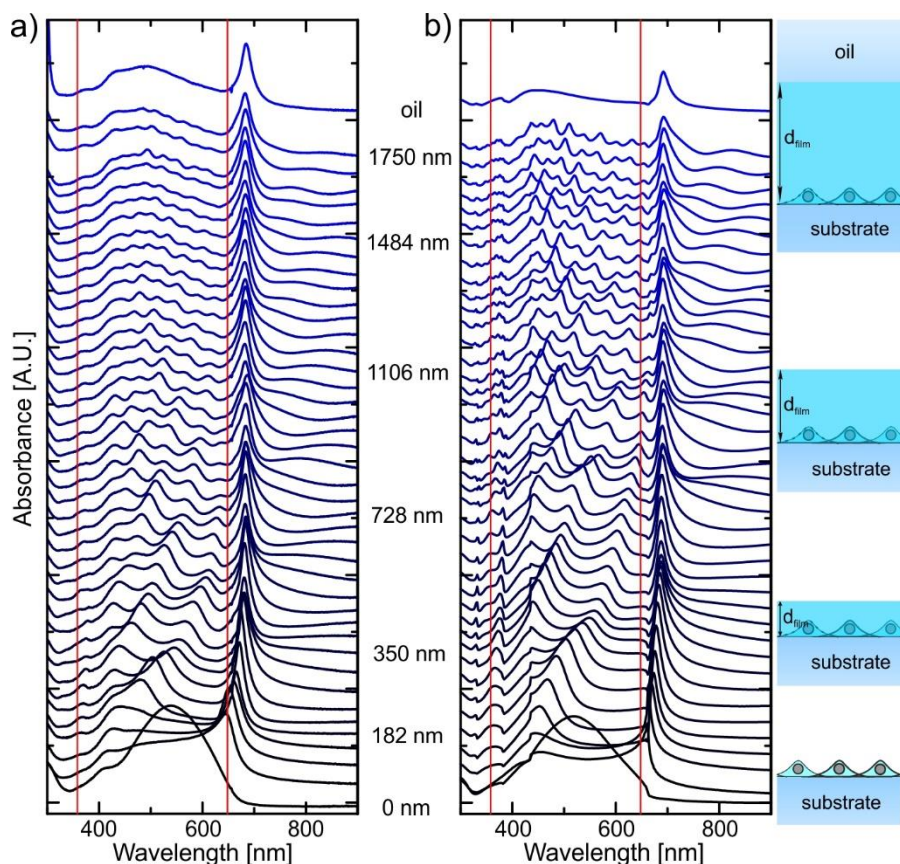


Figure 3. Influence of coating thickness on the optical response. (a) Experimental UV-vis spectra of a Ag-PNIPAM array ($d_{c-c} = 503$ nm) with increasing NOA coating thickness ranging from 0 to 1750 nm (black to blue traces) in 42 nm steps. The spectrum in blue at the very top corresponds to a sample top-coated with immersion oil. (b) Corresponding calculated spectra from FDTD. Vertical red lines indicate the LSPR region of the particle monolayer on glass (uncoupled state). Numbers in between both plots provide selected film thicknesses d_{film} at intermediate steps. Side view sketches on the right illustrate the sample structure for increasing film thicknesses d_{film} of the NOA coating.

We can conclude three key observations from Figure 3: (1) in an inhomogeneous RI environment without a RI matching top coating on the monolayer, the absorbance spectra reveal the dipolar LSPR of the silver nanoparticle cores with a very small quadrupolar contribution visible as a weak shoulder at lower wavelength. In this scenario, far-field plasmon resonance coupling is not present. (2) For an effectively infinite, homogeneous RI environment, that is, when the sample is additionally covered with oil, a sharp SLR as the result of plasmonic/diffractive coupling between the LSPR and the $\{1,0\}$ Bragg resonance of the lattice is observed at a wavelength slightly larger than the Bragg mode. Furthermore, a plasmonic contribution is observed as a broad resonance slightly blue-shifted as compared to the LSPR of the uncoupled system. (3) For finite size RI environments, that is, coatings with NOA, plasmonic/diffractive coupling is already enabled for thin NOA films leading to SLRs. The SLRs red-shift for thin, increasing coating thicknesses and reach a nearly constant wavelength

position for thicknesses equal to and larger than 392 nm. Additional resonances appear at lower wavelengths and increase in number with increasing coating thickness while also red-shifting. To analyze the findings for finite NOA film thicknesses with more detail, we mapped the center wavelength of all resonances that could be distinguished in dependence of the film thickness in Figure 4a.

Here, the red symbols belong to the experimentally measured peak positions, while the black symbols correspond to the positions from FDTD calculations. The LSPR region (uncoupled state) is highlighted as a gray area. Not only the observed trends in the evolution of the peak positions but also the absolute positions from the calculation nicely match the experimental data. The SLR (filled squares and upright triangles) red-shifts for thin NOA thicknesses and then remains constant with average values of $\lambda_{\text{SLR}}(\text{Ag-PNIPAM}) = 681$ nm in experiment and $\lambda_{\text{SLR}}(\text{Ag-PNIPAM}) = 691$ nm from the calculated spectra. The small deviation in SLR position can be explained by the positional disorder in the self-assembled sample of approximately 6 % (obtained by determination of d_{c-c} and standard deviation using AFM). This is in agreement with a study conducted by Augu   and Barnes, where the influence of disorder was studied using gold nanoparticle arrays prepared by electron-beam lithography and the coupled dipole model for simulation.⁵⁶ The additional higher order modes (open squares and upright triangles), which are located in the lower wavelength region, all start to form at approximately 415 nm and red-shift toward the SLR with increasing coating thickness. When approaching the {1,0} diffraction edge, the resonances get suppressed and vanish completely. This happens at shorter wavelengths in the experiment (640 nm) than in the simulation (670 nm) because in the experiment the SLR appears at slightly lower wavelengths. This leads to a small positional mismatch of the resonances between experiment and calculation close to the SLR, whereas all other resonance positions fit exceptionally well. The slightly different trend in peak shifts for the very first NOA coating steps (up to approximately 120 nm) will be discussed later on in this work together with results from Figure 4b. In Figure 4a also the {1,1} diffraction edge becomes clearly visible, and is responsible for the area without any resonance features between 390 nm and 415 nm. At even smaller wavelengths (350 – 390 nm) an additional set of resonances appears (circles and downward triangles) and red-shifts with increasing coating thickness. This is, in particular, visible in the calculated spectra. To obtain some deeper understanding on the origin of the higher order resonances, we also prepared plasmonic monolayer samples (i) using colloids with gold cores (Au-PNIPAM) that feature a LSPR at a significantly larger wavelength as compared to the colloids with silver cores and (ii) with the Ag-PNIPAM particles arranged with a significantly smaller center-to-center nearest neighbour distance ($d_{c-c} = 414$ nm) and thus

significantly blue-shifted Bragg resonances. A summary of the relevant sample parameters is provided in the Supporting Information in Table S1. Starting with the Au-PNIPAM monolayer (Figure 4b), that has very similar inter-particle distances ($d_{c-c} = 510$ nm) than the previous Ag-PNIPAM sample ($d_{c-c} = 503$ nm) in Figures 3 and 4a, we see a very similar trend for all resonances. Full spectra for each coating step can be found in the Supporting Information in Figure S3. Looking at Figure 4b, again the data from experiment (red symbols) and simulation (black symbols) match nicely. The SLR (filled upright triangles and squares) red-shifts for thin NOA thicknesses until reaching constant values of $\lambda_{\text{SLR}}(\text{Au-PNIPAM}) = 698$ nm in the experiment and $\lambda_{\text{SLR}}(\text{Au-PNIPAM}) = 700$ nm from FDTD simulations. At the same time a single, second resonance at lower wavelengths decreases in wavelength for both samples until reaching a minimum and then starting to increase. This initial blue shift of the second resonance, below a certain coating thickness, can be explained by the fact that energy conservation must be complied while the coupling strength increases and the SLR redshifts.¹³ We attribute these features to a purely plasmonic contribution. When the NOA coating is thick enough to enable the strongest plasmonic/diffractive coupling, the scenario changes. On the one hand, the lower wavelength features start to increase in wavelength with increasing NOA thickness and on the other hand more resonances appear in the LSPR region of the respective plasmonic material. As discussed earlier, these higher order resonances increase in number and red-shift with increasing NOA thickness, while they vanish when approaching the $\{1,0\}$ diffraction edge. The striking difference when comparing the spectral features of the Ag-PNIPAM array (Figure 4a) and Au-PNIPAM array (Figure 4b) is the spectral region in which the higher order modes appear. For silver, the features are distributed over a wide wavelength range from 410 nm to 650 nm. In the case of gold, the features only become intense at approximately 500 nm up to 650 nm (experiment) or 680 nm (FDTD).

We observe that pronounced higher order resonances are supported in the respective LSPR region (gray areas) of the individual plasmonic components (uncoupled state). At the same time, these resonances vanish when approaching diffraction edges. This is clearly observed for the $\{1,0\}$ diffraction edge as an upper wavelength limit and also in the intermediate wavelength range close to the $\{1,1\}$ diffraction edge. We now want to address the optical response of the Ag-PNIPAM sample with a smaller inter-particle distance of $d_{c-c} = 414$ nm summarized in Figure 4c. Full spectra can be found in the Supporting Information, Figure S4. Because of the smaller lattice spacing, the SLR resonances (filled symbols) appear significantly blue-shifted as compared to the previously discussed samples with larger interparticle distances.¹⁹ After an initial red-shift of the SLR with increasing NOA thickness, constant values of approximately

$\lambda_{\text{SLR}}(\text{Ag-PNIPAM}) = 600 \text{ nm}$ are obtained. Higher order modes that increase in number and red-shift with increasing coating thickness can be detected again, but as in the case of the SLR, at lower wavelengths than for the larger period. Thus, it becomes obvious that not only the SLR but also the higher order resonances are directly correlated with the lattice spacing. Also, the higher order resonances start at a much lower wavelength of approximately 350 nm because the $\{1,1\}$ diffraction edge is now at much shorter wavelength of approximately 318 nm as compared to 388 nm for the Ag-PNIPAM lattice with $d_{\text{c-c}} = 503 \text{ nm}$. Apart from this, a feature at 410 nm is visible in all spectra independent of the coating thickness. We assign this to a weak quadrupolar contribution of the silver particle LSPR. A direct comparison of the peak positions for Ag-PNIPAM and Au-PNIPAM is given in the Supporting Information, Figure S5a and a comparison of the Ag-PNIPAM monolayers with different lattice periods in Figure S5b.

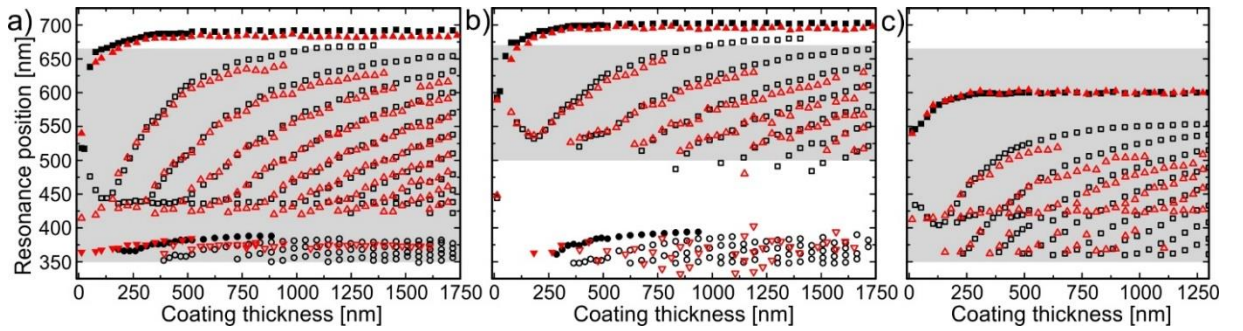


Figure 4. Influence of coating thickness on resonance positions from calculated (black symbols) and experimental spectra (red symbols) as a function of the NOA thickness ranging from 13 to 1750 nm. (a) Ag-PNIPAM array with $d_{\text{c-c}} = 503 \text{ nm}$. (b) Au-PNIPAM array with $d_{\text{c-c}} = 510 \text{ nm}$. (c) Ag-PNIPAM array with $d_{\text{c-c}} = 414 \text{ nm}$. The gray area in each plot indicates the LSPR region of the respective particle monolayer on glass against air (uncoupled state). Filled symbols describe in-plane coupling to $\{1,0\}$ (squares, upright triangles) and $\{1,1\}$ (circles, downward triangles). Open symbols correspond to higher order modes: first set with squares and upright triangles, second set with circles and downward triangles.

Correlation between Higher Order Resonances and Lattice Diffraction

Knowing that the positions of the higher order resonances in the LSPR region of the respective plasmonic particles depend on the lattice period for a given NOA thickness and at the same time red-shift with increasing NOA thickness for a given lattice period, we assume that 3D diffraction is responsible for this behavior. In this case, the plasmonic particle monolayer dictates the lattice period in x and y and the distance between the plasmonic monolayer (measured from the scattering plane) to the NOA/air interface defines the period in z (compare Figure 1b,c). The corresponding diffraction equation for a 3D hexagonal lattice is⁵⁴⁻⁵⁵

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (3)$$

Here, d is the interplanar spacing, h, k, l the Miller indices, a the in-plane lattice constant (d_{c-c} like in eq. 1) and c the out-of-plane lattice constant:

$$c = 2 \cdot (d_{film} - 65 \text{ nm}) \quad (4)$$

The definition of c takes into account the following considerations: All spectroscopic measurements in this work were done under normal incidence. Thus, apart from some reflective losses at the air/NOA interface, a plane wave travelling through the NOA film incidents on the plasmonic particle lattice normal to the lattice plane. Here, light is scattered by the plasmonic particles including significant backscattering into the NOA film. This backscattered light is then partially reflected at the air/NOA interface until reaching again the particle lattice (mirror-like behavior). Here, we assume that the RI difference between the coating and air determines the strength of the mirror effect, that is, the backscattering efficiency. A high RI contrast leads to stronger backscattering and thereby a higher intensity of the coupling modes, whereas low differences in RI should lead to a weaker backscattering effect. Consequently, the light scattered first at the particle lattice travels two times the distance from the particle center at $z = 65 \text{ nm}$ to the air/NOA interface at $z = d_{film}$ (see sketch Figure 1c). With the interplanar spacing d from eq 3 and the RI, we now get access (see eq 2) to the wavelength of diffraction in 3D λ_{hkl} .

In Figure 5a,c,e we plotted exemplary spectra of the three, previously discussed lattices (see Figure 4) for a NOA thickness of approximately 728 nm. Again, the nice agreement in peak position and also intensity between the experiment (red traces) and simulation from FDTD (black traces) is visible. The calculated 3D Bragg resonances λ_{hkl} from eqs 2 - 4 are highlighted as gray and black dashed, vertical lines. One can observe that the calculated and measured peaks appear at slightly larger wavelength than the calculated Bragg resonances, indicative for plasmonic/diffractive coupling. Figure 5b,d,f) summarizes all spectra for various coating thicknesses as obtained from FDTD in absorbance maps with the coating thickness as the x -axis and the wavelength as y -axis. The solid lines show the development of the calculated Bragg resonances in dependence of coating thickness. To calculate the Bragg resonance position for thin coatings, an averaged RI was used in eq 2. This takes into account the thickness-dependent RI contribution of the glass substrate, NOA layer, and air for the calculation of the Bragg mode into account (for details see Supporting Information Figure S6). After a thickness of approximately 450 nm, the RI change became insignificant, that is, the environment is

homogeneous in RI with respect to the lattice/scattering plane. This assumption is supported by the fact that the SLRs from coupling to the $\{1,0\}$ diffraction edges reach constant values for thicknesses in this range and higher. Thus, a constant value of 1.54 was used for the calculation corresponding to thicker NOA coatings.

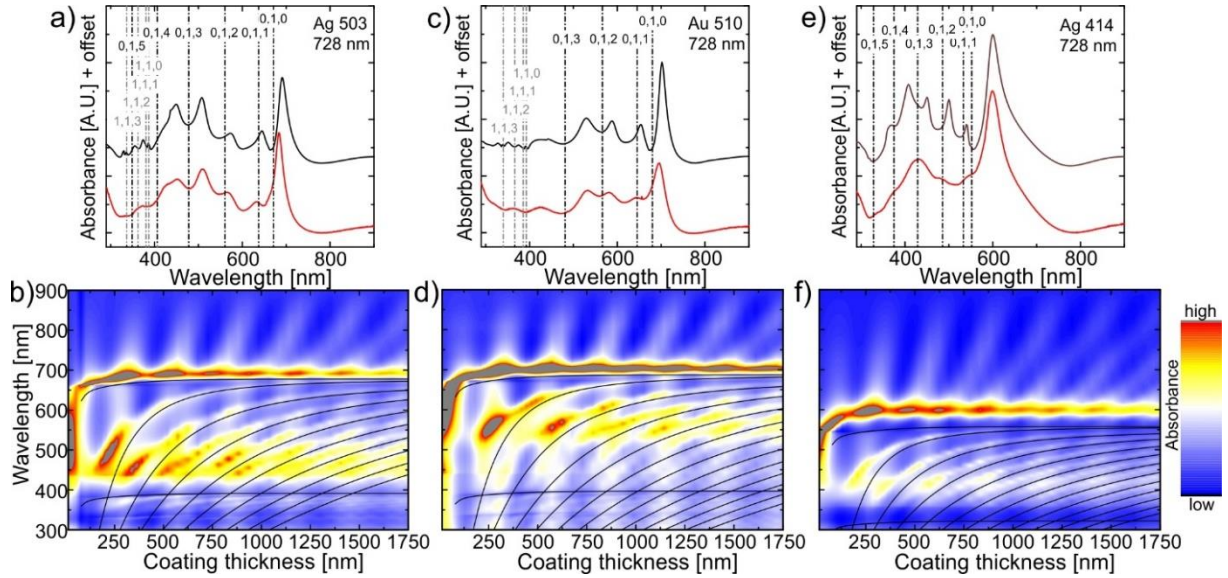


Figure 5. Correlation between 3D diffraction and observed resonances. Results for an Ag-PNIPAM lattice $d_{c-c} = 503$ nm (a and b), an Au-PNIPAM lattice with $d_{c-c} = 510$ nm (c and d) and an Ag-PNIPAM lattice with $d_{c-c} = 414$ nm (e and f). UV-vis absorbance spectra for samples with NOA thicknesses of approximately 728 nm from the experiment (red traces) and from FDTD calculations (black traces) with vertical lines corresponding to calculated Bragg diffraction wavelengths (gray lines: 1,1,x group; black lines: 0,1,y group) are presented in (a,c,e). Absorbance maps of calculated spectra with diffraction modes (black lines) are shown in (b,d,f).

All resonances from the FDTD calculation nicely follow the evolution of the theoretical Bragg resonances, again with a small wavelength offset due to the coupled nature of the modes. Consequently, we propose that higher order SLRs can also be supported in our samples when the out-of-plane Bragg modes spectrally overlap with the LSPR region of the individual plasmonic building blocks. Apart from these out-of-plane modes, the absorbance maps in Figure 5b,d,f show additional dispersive modes at a wavelength larger than the SLRs from coupling to the $\{1,0\}$ diffraction edges. The spectral positions of these modes are independent from the particle lattice, that is, the lattice spacing and particle material. This independence is demonstrated in the profile plots in the Supporting Information Figure S7. In contrast, we find a linear dependence on the film thickness and therefore attribute thin film interference effects to be the origin of these dispersive modes. This interference can occur, despite excitation normal to the film, due to angular scattering from the particles enabling thin film interference.⁵⁷ When

the interference modes cross the SLRs at specific coating thicknesses, further field enhancement is observed and the SLRs appear more intense.

Free-Standing Plasmonic Monolayer Films

Taking advantage of the fact that pronounced SLRs from coupling to the $\{1,0\}$ diffraction edge can already be observed in finite size RI environments, we prepared free-standing, sub-micrometer thick polymer films with embedded silver nanoparticle arrays: as a starting point, a ZnO sacrificial layer was prepared on a glass substrate. Then, an approximately 450 nm thick film of NOA was applied by spin-coating followed by the collection of an Ag-PNIPAM monolayer ($d_{c-c} = 492 \pm 27$ nm) from the air/water interface. An AFM height profile of the monolayer can be found in the Supporting Information (Figure S8a). To finish the film preparation, an approximately 450 nm thick film of NOA was applied on top of the Ag-PNIPAM monolayer. A sketch of the sample structure is shown in Figure 6a, and further details of the preparation can be found in the Experimental Details section. By immersion of the sample into an HCl solution (pH 1) the ZnO sacrificial layer was slowly dissolved (Figure 6b) and the Ag particle array sandwiched between the two NOA films was carefully moved to the air/water interface. The freely floating film was collected with a 3D printed film holder (Figure 6c). The photographs in Figure 6d,e show the dried, macroscopic free-standing film with an embedded silver particle array as seen in transmission (e) and reflection (d). The photograph taken from the side in reflection (Figure 6d) reveals the strong opalescence of the periodic particle monolayer over the entire film caused by the Bragg reflection of the periodic silver nanoparticle array with a visible wavelength scale interparticle distance. In contrast, in the top-view photograph recorded in transmission (Figure 6e), the sample appears highly transparent. UV-vis absorbance spectra of the NOA sandwiched monolayer prior to removal from the ZnO-coated glass substrate (black trace) and after transfer to the film holder (red trace) are shown in Figure 6f. Both spectra feature pronounced SLRs at 673 nm and 676 nm on the ZnO-coated glass substrate and from the free-standing film, respectively.

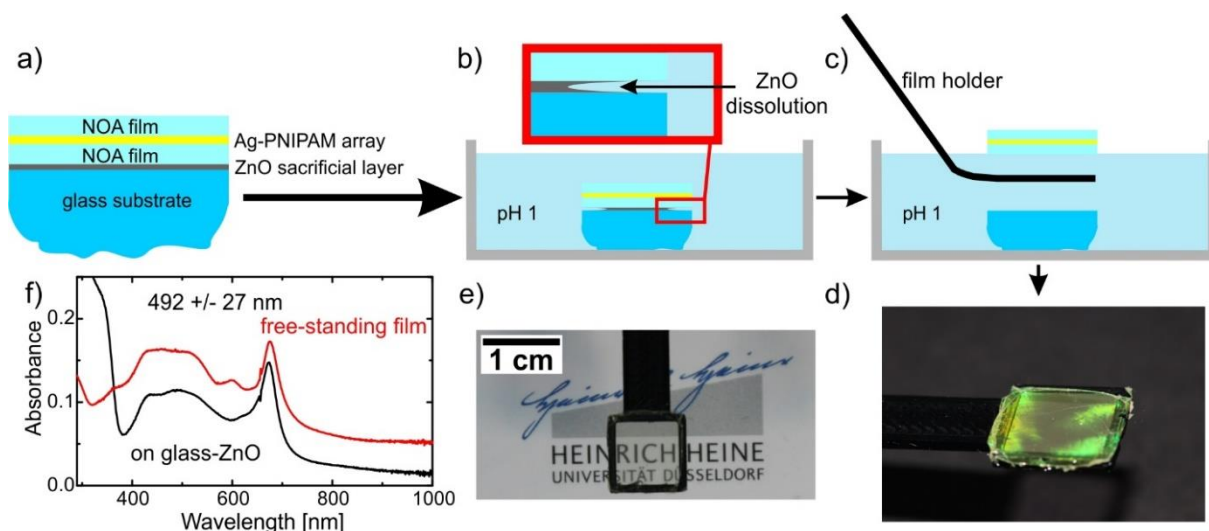


Figure 6. Fabrication and characterization of the free-standing NOA-embedded Ag particle array. (a) Starting structure on a glass substrate with a ZnO sacrificial layer (grey) and the NOA/Ag-PNIPAM monolayer/NOA film. (b) Structure immersed in aqueous HCl solution (pH 1). The ZnO layer is slowly dissolved. (c) Completely detached NOA/Ag-PNIPAM monolayer/NOA film at air/water interface and transfer to support structure (film holder). (d) Digital photograph taken at an angle (reflection) of the film supported on a 3D-printed PET frame. (e) Digital photograph of the sample placed over the university logo in transmission geometry. (f) UV-vis absorbance spectra of embedded particle array on the glass/ZnO/NOA substrate (black trace) and after transfer to support structure (red trace). The embedded Ag-PNIPAM monolayer has a $d_{c-c} = 492 \pm 27$ nm.

This indirectly manifests that the particles and NOA films were not degraded by the acid-treatment used for the detachment of the film from the glass substrate. The reproducibility of the process is demonstrated in the Supporting Information, Figure S8b where the UV-vis absorbance spectra of another Ag-PNIPAM sample ($d_{c-c} = 509 \pm 33$ nm) are shown. Thus, we have successfully demonstrated that free-standing polymer films with embedded periodic plasmonic nanostructures featuring SLRs can be produced with centimeter-scale dimensions. In fact, taking into account the size of the free-standing film, one can calculate the number of embedded silver nanoparticles to approximately 4×10^8 . We want to highlight that the overall thickness of the film is below $1 \mu\text{m}$. Thus, our approach represents an important step towards miniaturization (in z -direction) of optically functional materials that are desirable in fields like sensing and nanolasers.

Conclusions

In summary, we have elucidated the optical response of plasmonic nanoparticle arrays in finite-thickness polymer films that support the formation of SLRs. For this, we used wet-chemically synthesized Ag-PNIPAM and Au-PNIPAM core/shell colloids that were self-assembled in periodic, hexagonally ordered monolayers on glass substrates. An increasingly thick polymer coating (NOA) matching closely the RI of the glass substrate was applied by multiple spin-

coating steps (0 – 1750 nm). By doing so, we were able to distinguish between RI-dependent effects that mainly affect the formation and resonance position of in-plane SLRs, and film thickness dependent features. The effect of the RI environment is only visible at thin polymer coatings leading to red-shifts of the resonances. When reaching an effectively homogeneous RI in the near-field zone of the plasmonic particles, the SLRs remain at constant wavelengths. A further increase of coating thickness has almost no impact on this resonance. This allowed us to prepare a free-standing plasmonic nanoparticle array embedded in a sub-micron thick NOA film environment, which shows pronounced plasmonic/diffractive coupling.

Apart from SLRs, we observed higher order resonances that show pronounced red-shifts with increasing NOA thickness, even for very thick coatings. The resonances result as a consequence of out-of-plane diffraction and coupling to the particles' LSPRs. Consequently, the wavelength of these resonances depends on the coating thickness, the plasmonic material, and the interparticle spacing in the array. All findings were in good agreement with FDTD simulations. Our work contributes to a deeper understanding of optical effects in plasmonic nanoparticle arrays, in particular in confined spaces, and additionally demonstrates the possibility of device miniaturization in *z*-direction by the preparation of free-standing plasmonic films. Interestingly, a recent study showed that lattices of 200 particles already support reasonably good SLRs⁵⁸ and earlier Rodriguez *et al.*⁵⁹ reported that 20 – 30 particles in linear particle array are sufficient to support SLRs with high quality factors. Assuming periodicities of 500 nm, this would result in array sizes as small as 10 x 10 μm^2 . Consequently, combining our findings with the possibility of reducing the sample dimensions in the *x-y* lattice plane presents a promising route to device miniaturization in 3D.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supporting Information

Characterization of Au-PNIPAM Core/Shell Particles

Figure S1a shows a bright field TEM image of the Au-PNIPAM core/shell particles. The spherical gold cores have an average diameter of $d_{\text{core}} = 100 \pm 7$ nm. The collapsed PNIPAM shell is visible as grey corona surrounding the black, high contrast cores. These particles were self-assembled at the air/water interface and collected on a glass substrate. An AFM image of the resulting hexagonally ordered monolayer is depicted in Figure S1b and a $d_{\text{c-c}}$ of 510 ± 24 was determined.

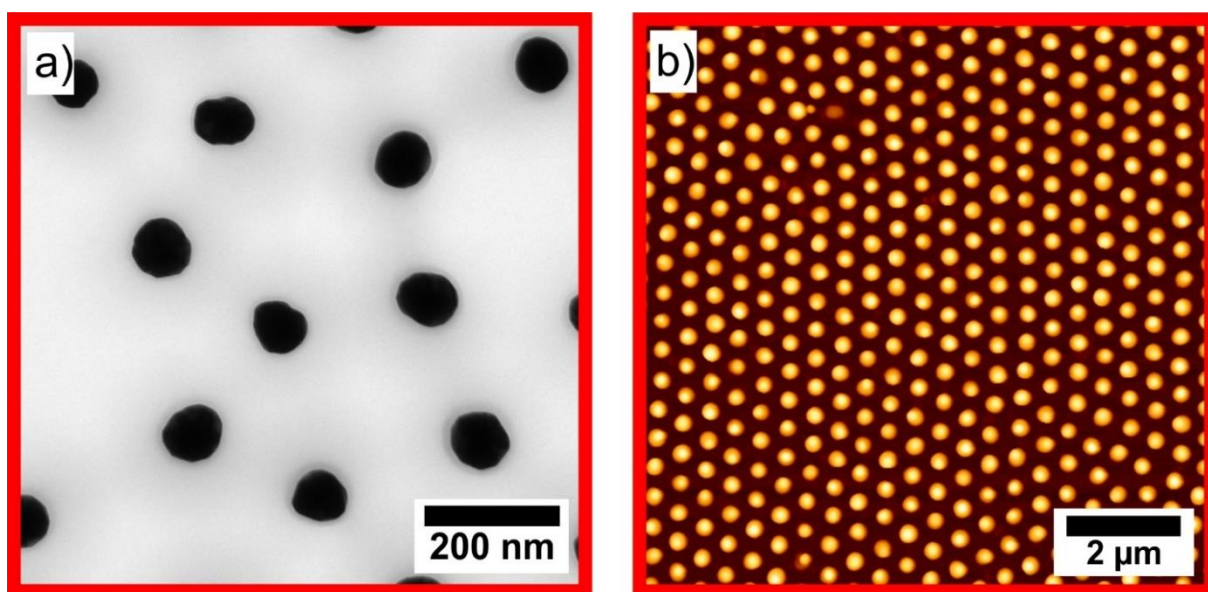


Figure S1. Characterization of Au-PNIPAM core/shell particles. (a) Bright field TEM image. (b) AFM height profile image of particles self-assembled into a hexagonally ordered monolayer on glass substrate.

Topographical Characterization of the Monolayers and the NOA Coating

The AFM height image in Figure S2a was used to determine the average height of a particle monolayer by measuring the height profile of approximately 30 individual particles. An exemplary height trace is presented in Figure S2c and the underlying dried particle structure is depicted schematically with a 100 nm Ag core (gray) and the collapsed PNIPAM shell (green) around the core. This dry PNIPAM shell has a RI of approximately 1.49. Since it is directly in the near field zone of the nanoparticle it also influences the LSPR wavelength. The AFM image in Figure S2b was used for the determination of the surface roughness of a bare NOA film. A RMS roughness of 0.5 nm and a peak-to-valley roughness of 2.9 nm was calculated.

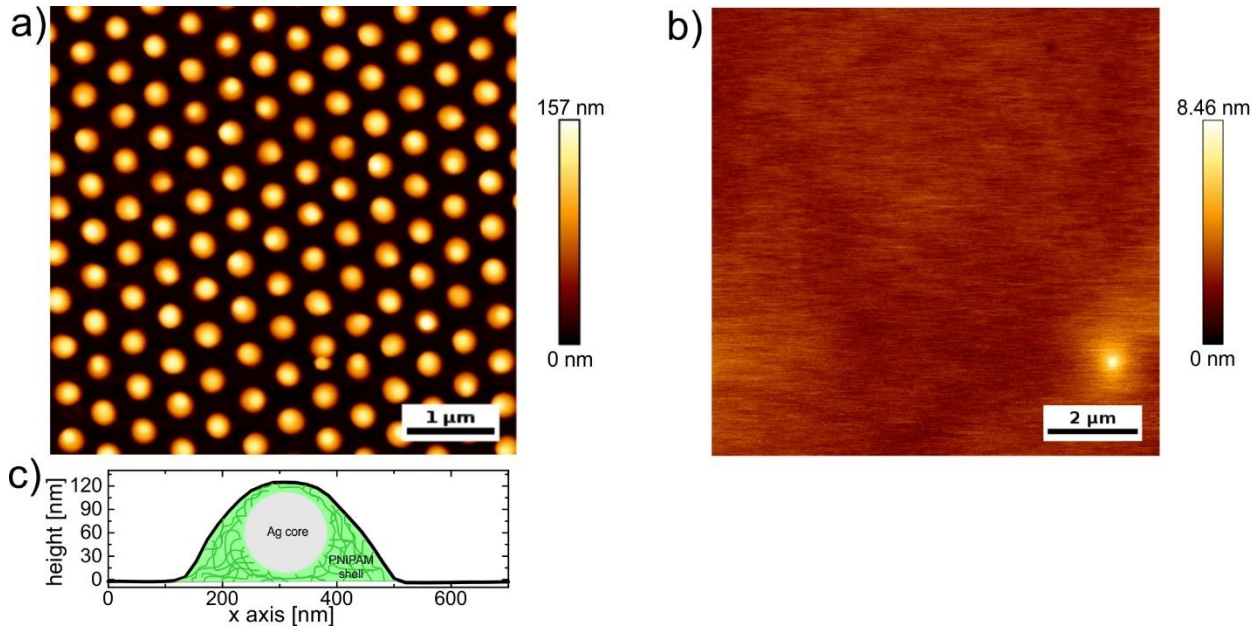


Figure S2. AFM analysis of particle monolayer and NOA film. (a) AFM height image of Ag-PNIPAM particle array with $d_{c-c} = 503 \pm 27$ nm. (b) AFM height image of NOA film on glass without particle array. (c) Representative height profile of a particle from the monolayer shown in (a) with a schematic core-shell particle sketch to demonstrate the structure.

Characterization of Hexagonally Ordered Nanoparticle Monolayers

Table S1 summarizes the basic information of the three analyzed monolayers. The nearest neighbor center-to-center distance d_{c-c} , the interplanar spacing $d_{(0,1)}$, the LSPR of the particles in dispersion $\lambda_{\text{LSPR-disp}}$ and of the monolayer on glass against air $\lambda_{\text{LSPR-air}}$ as well as the SLR of the monolayer in a homogenized RI environment $\lambda_{\text{SLR-hom}}$ is given for the two Ag-PNIPAM and the Au-PNIPAM monolayers.

Table S1. Summary of structural and optical parameters of monolayer samples on glass used throughout the present study. Nearest neighbor center-to-center distance d_{c-c} , interplanar spacing $d_{(0,1)}$, the LSPR of the particles in dispersion $\lambda_{\text{LSPR-disp}}$, of the monolayer against air $\lambda_{\text{LSPR-air}}$ and the SLR of the monolayer in a homogenized RI environment $\lambda_{\text{SLR-hom}}$.

Cores/shell sample	d_{c-c} [nm]	$d_{(0,1)} = \frac{\sqrt{3}}{2} * d_{c-c}$ [nm]	$\lambda_{\text{LSPR-disp}}$ [nm]	$\lambda_{\text{LSPR-air}}$ [nm]	$\lambda_{\text{SLR-hom}}$ [nm]
Ag-PNIPAM	503 ± 27	436 ± 23	505.5	538.5	681
Au-PNIPAM	510 ± 24	442 ± 21	578.5	588	698
Ag-PNIPAM	414 ± 25	358 ± 22	505.5	539.5	600

The interplanar spacing d for a hexagonal crystal system is given by:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (\text{S-1})$$

Here h , k and l are the Miller indices and a is the in-plane lattice constant. For our particle arrays a corresponds to the nearest neighbor center-to-center interparticle distance d_{c-c} . c is the out-of-plane lattice constant. In our samples c corresponds to two times the distance between the scattering plane (particle lattice, center position in z -direction) and the NOA/air interface. For $l = 0$ or very thick NOA coatings/the extreme case of oil as a superstrate, $c \gg a$ and thus equation (S-1) simplifies to:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) \quad (\text{S-2})$$

Equation (S-2) can now be used to calculate the interplanar spacing for the 2D diffraction case, i.e. where out-of-plane diffraction is not observed.

UV-vis Absorbance Spectra of Au-PNIPAM ($d_{c-c} = 510$ nm) and Ag-PNIPAM ($d_{c-c} = 414$ nm) Arrays

Figure S3 and S4 show experimental (a) and calculated (b) UV-vis absorbance spectra of the Au-PNIPAM ($d_{c-c} = 510$ nm) and Ag-PNIPAM ($d_{c-c} = 414$ nm) monolayer samples, respectively. In both diagrams the spectra start from the bottom with the monolayer on glass without NOA coating (black spectrum) and proceed up to the top to a coating thickness of approximately 1750 nm (Au-PNIPAM $d_{c-c} = 510$ nm, second spectrum from top) or 1250 nm (Ag-PNIPAM $d_{c-c} = 414$ nm, second spectrum from top). In addition, spectra recorded after an additional top coating with immersion oil providing an effectively infinite RI environment are shown as the last spectra at the top (green).

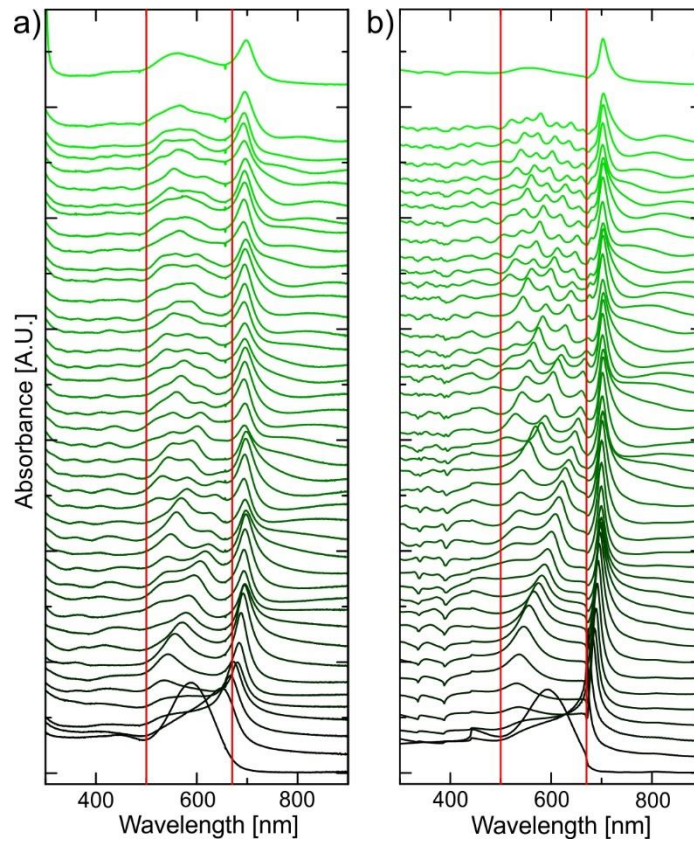


Figure S3. Influence of coating thickness on optical response of an Au-PNIPAM monolayer on glass. (a) Experimental UV-vis absorbance spectra of Au-PNIPAM array with $d_{c-c} = 510$ nm and (b) corresponding calculated spectra from FDTD for increasing NOA coating thickness ranging from 0 to 1750 nm (black to green traces) in 42 nm steps. The spectrum in green at the very top corresponds to a sample top-coated with immersion oil.

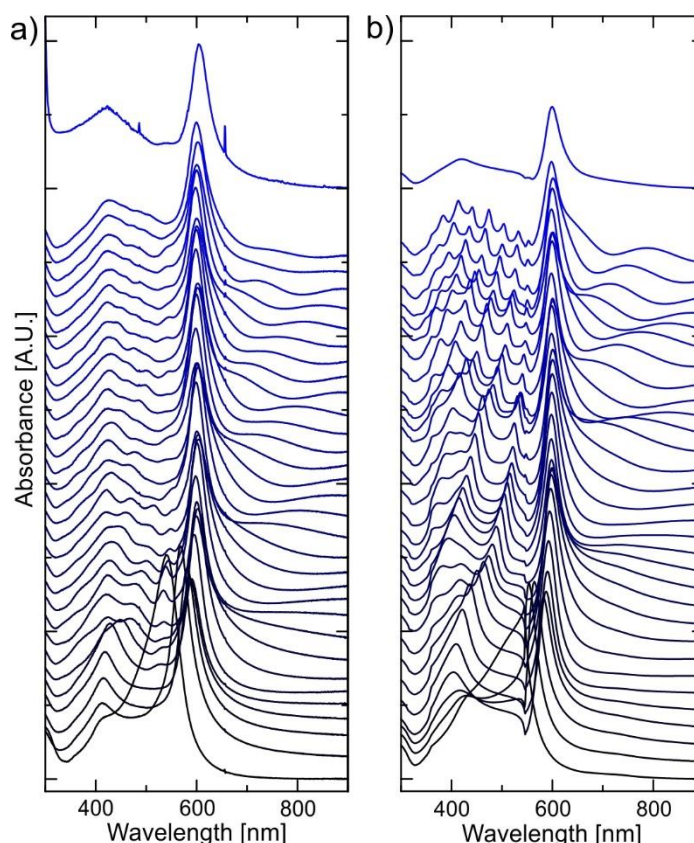


Figure S4. Influence of coating thickness on optical response of an Ag-PNIPAM monolayer on glass. Experimental UV-vis absorbance spectra of (a) Ag-PNIPAM array with $d_{c-c} = 414$ nm and (b) corresponding calculated spectra from FDTD for increasing NOA coating thickness ranging from 0 to 1250 nm (black to blue traces) in 42 nm steps. The spectrum in blue at the very top corresponds to a sample top-coated with immersion oil.

Influence of Plasmonic Material and Interparticle Spacing on Resonance Position

Figure S5a shows a direct comparison of the experimentally determined peak positions for an Ag-PNIPAM and an Au-PNIPAM monolayer. The influence of the LSPR area can be directly seen. For the Ag-PNIPAM sample resonances can be detected from 410 to 650 nm whereas the Au-PNIPAM sample features pronounced resonances from 500 nm to 650 nm. This coincides with the respective LSPR areas. In Figure S5b a comparison of the experimentally determined peak positions for Ag-PNIPAM monolayer samples with different lattice periods is presented. For a given NOA thickness all observable resonances are significantly blueshifted for the sample with smaller period due to the blueshifted Bragg resonance positions.

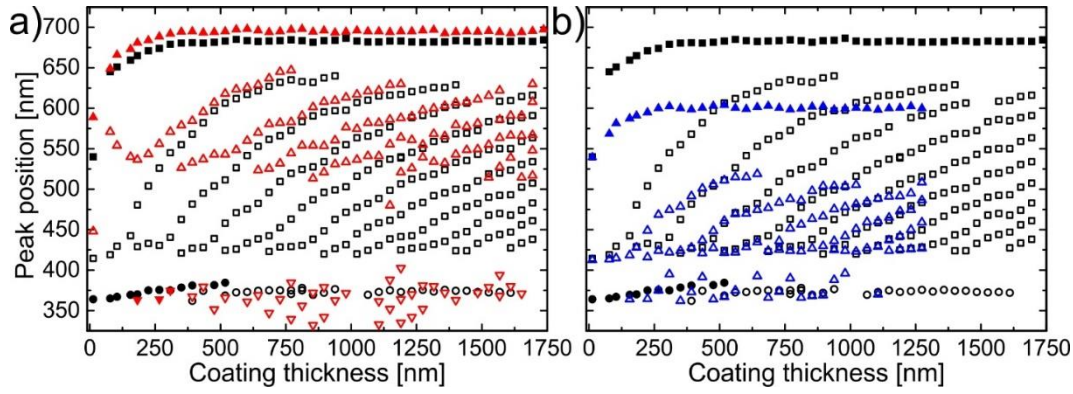


Figure S5. (a) Experimental resonance positions as a function of the NOA thickness for an Ag-PNIPAM monolayer (black symbols, $d_{c-c} = 503$ nm) and an Au-PNIPAM monolayer (red symbols, $d_{c-c} = 510$ nm). (b) Experimental resonance positions for Ag-PNIPAM monolayers with $d_{c-c} = 503$ nm (black symbols) and $d_{c-c} = 414$ nm (blue symbols). Filled symbols describe in-plane coupling to $\{1,0\}$ (squares, upright triangles) and $\{1,1\}$ (circles, downward triangles). Open symbols correspond to higher order modes: First set with squares and upright triangles. Second set with circles and downward triangles.

Determination of Average RI for Different Coating Thicknesses

We performed FDTD simulations for a periodic Ag-PNIPAM monolayer with $d_{c-c} = 503$ nm in a homogeneous, infinite RI environment (RI 1.250 to 1.575 in 0.025 steps). The thereby accessible SLR positions show a linear dependence on the RI as shown in Fig S6a.

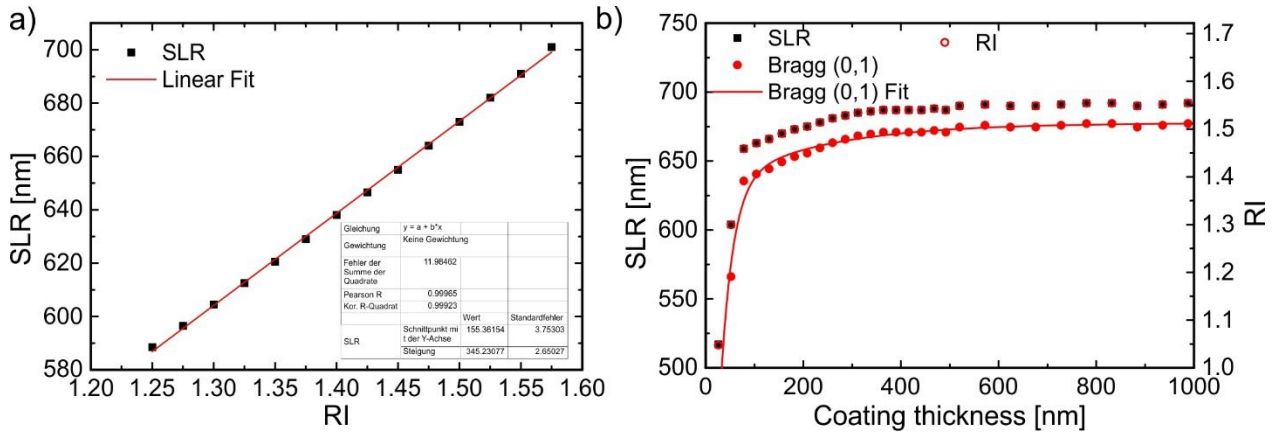


Figure S6. Extraction of coating thickness-dependent average RI from calculated data. (a) Linear dependence of SLR wavelength on RI for an infinite, homogeneous environment. The red solid line is a linear fit to the data. (b) SLR and $\{0,1\}$ Bragg mode position (left y-axis, black solid squares and red solid spheres) and RI (right y-axis, red open spheres) as a function of coating thickness. The red solid line is an interpolation of the Bragg wavelength data (red circles).

This dependence was used in order to estimate the average, effective RI corresponding to the experimentally determined SLR position for monolayer samples with different thicknesses of the NOA coating. The results are shown in Figure S6b with the respective resonance position as the left y-axis and the corresponding RI matching the experimental SLR wavelength plotted as right y-axis. The RI values were used to calculate the $\{0,1\}$ diffraction mode wavelength

(red filled spheres) for each of the experimental coating thicknesses according to equation 2 of the main manuscript. The red solid line shows an interpolation to the data in order to obtain the RI continuously for the full range of thicknesses.

Thin Film Interference in the Long Wavelength Range

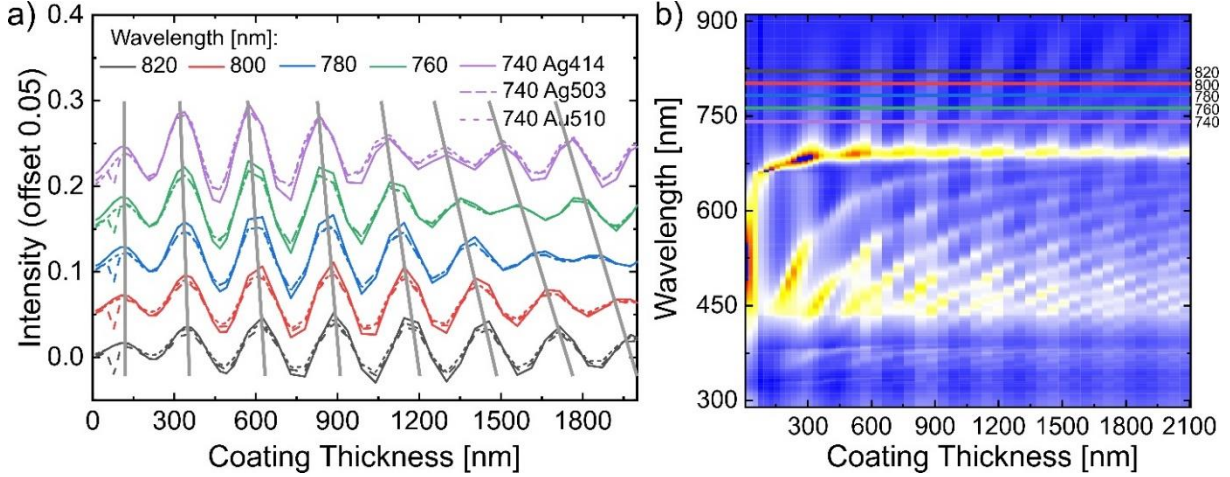


Figure S7. Profile plots of long wavelength range features. (a) Line profiles from 740 nm to 820 nm (violet to black trace) for Ag-PNIPAM with $d_{c-c} = 414$ nm (solid lines), Ag-PNIPAM with $d_{c-c} = 503$ nm (long dashed lines) and Au-PNIPAM with $d_{c-c} = 510$ nm (short dashed lines). The grey lines are guides to the eyes indicating the mode shift in dependence of wavelength. (b) Exemplary absorbance map of Ag-PNIPAM with $d_{c-c} = 503$ nm showing the position of the profile lines in (a).

Additional Characterization of Free-Standing Plasmonic Monolayer Films

Figure S8a) shows an AFM image of an Ag-PNIPAM monolayer deposited on a glass substrate with a ZnO/NOA coating. The hexagonal order is clearly visible and a d_{c-c} of 492 ± 27 nm was determined. Apart from this sample and the respective spectra showing pronounced SLRs in Figure 6f of the main manuscript, another free-standing SLR sample was prepared. The corresponding UV-vis spectra of this sample are shown in Figure S8b). The d_{c-c} of this Ag-PNIPAM sample is 509 ± 33 nm and the SLR is located at 688 nm on the glass/ZnO/NOA substrate and at 692 nm in the free standing NOA film.

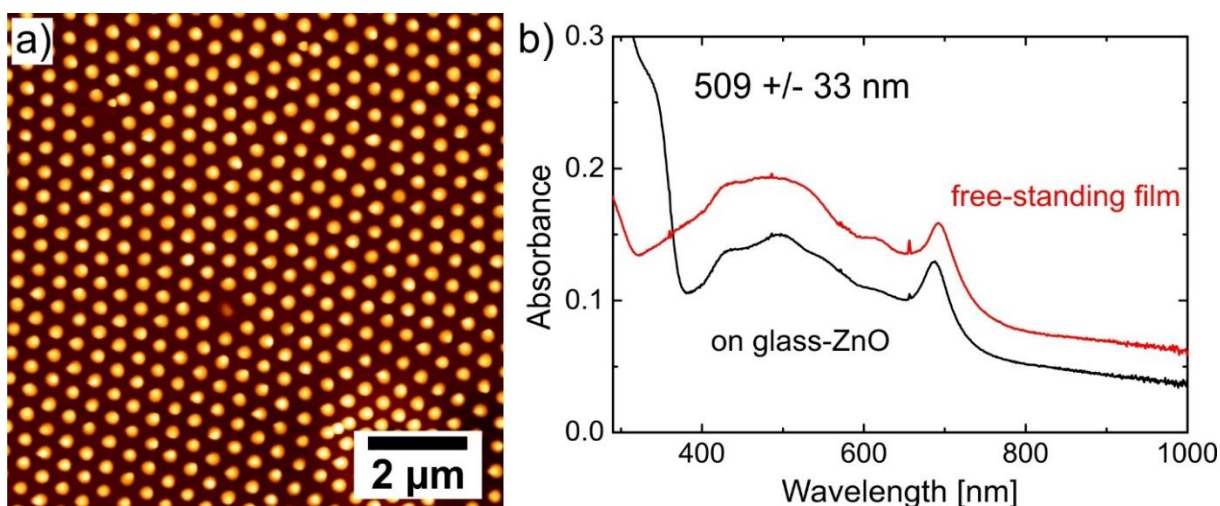


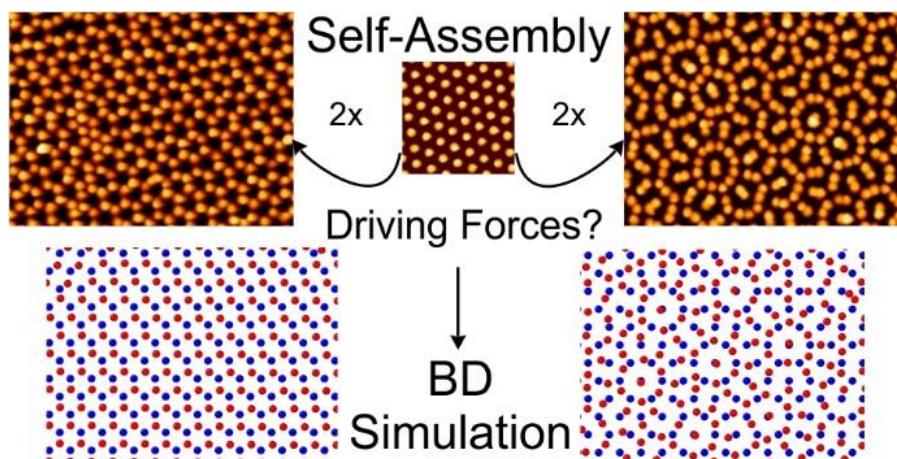
Figure S8. (a) AFM height image of hexagonally ordered Ag-PNIPAM particle array ($d_{c-c} = 492 \pm 27$ nm) deposited on top of a NOA film. (b) UV-vis absorbance spectra of an Ag-PNIPAM particle array ($d_{c-c} = 509 \pm 33$ nm) sandwiched between NOA on the glass/ZnO substrate (black trace) and in a free-standing film after transfer to the film holder (red trace).

7 Moiré and honeycomb lattices through self-assembly of hard-core/soft-shell microgels: experiment and simulation

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Abstract

Control over microstructure and interparticle spacing in substrate-supported colloidal arrangements is a key challenge in colloidal self-assembly. We demonstrate here the preparation of Moiré and honeycomb monolayer lattices from core/shell microgels with rigid inorganic cores and soft, deformable hydrogel shells. These structures were realized by the sequential double deposition of freely floating monolayers from the air/water interface onto the same, centimetre-scale substrate. Due to the soft and deformable character of the hydrogel shells, the second applied monolayer fully settles into the same plane as the first monolayer. The resulting structural motif is determined by the drying conditions applied to the second deposition step. We support our experimental findings by Brownian dynamics simulations and provide insights into the structure formation process.

Introduction

Colloidal self-assembly has seen tremendous progress in recent years due to developments in the synthesis of colloids with size and shape control on the one hand and in self-assembly methods on the other hand.^{1–13} An ongoing challenge in this field is to fully explore the structural diversity that can be accessed by self-assembly of simple colloidal building blocks,^{14–19} ideally from stable “colloidal inks”. Furthermore, the application to functional colloids, *e.g.* noble metal nanoparticles that feature localised surface plasmon resonances (LSPRs), is relevant to fields such as light-management in thin-film solar cells,²⁰ fabrication of new optical metamaterials²¹ and sensors²² as well as 2D nanolasers.^{23–27} Control over surface coverage, homogeneity, inter-particle distance and periodicity are crucial criteria relevant to such applications.²⁰ An example for a versatile assembly strategy is interface-mediated assembly using *e.g.* air/water interfaces where initially hexagonal close packed arrays of hard colloids with large single crystalline domains were achieved.^{28–30} Recently this process was extended by Hummel *et al.* who showed that all five 2-dimensional Bravais lattices are accessible by transfer of particle monolayers from air/water interfaces onto substrates with defined contact angles.³¹ Here non-close packed assemblies became accessible by the post-assembly lattice deformation. In contrast to the assembly of hard sphere colloids, soft particles have recently attracted a lot of attention due to their soft interaction potential^{32–35} and the resulting deformability.^{36,37}

Furthermore, it is possible to combine functional hard sphere-like colloids that feature *e.g.* plasmonic or fluorescent properties with soft polymer materials in form of well-defined core/shell colloids.^{38,39} In this case particle–particle interactions are determined by the soft polymer shell that also controls the inter-particle distance in assembly.²⁸

Volk *et al.* have shown that hydrogel encapsulated silver and gold nanoparticles can spontaneously self-assemble into hexagonally packed monolayers when floated at the air/water interface.¹⁴ The resulting structures showed a homogeneous surface coverage independent of the size and material of the employed plasmonic core. The interparticle distances were purely determined by the shell size and the time-dependent shell expansion at the air/water interface. Starting with interparticle distances close to the bulk hydrodynamic diameter right after deposition of the particles to the air/water interface, interfacial tension causes lateral deformation of the hydrogel shells leading to an increase in interparticle distance with time.

This assembly concept has been extended by Honold *et al.* who showed that the sequential double deposition of core/shell colloids from air/water interfaces onto solid supports can lead to binary monolayers with honeycomb structures.⁴⁰ Here the particles from the second deposition can settle into the large voids from the first deposition. Upon drying the shell shrinks to a much smaller size on the substrate leaving large voids in between the particles. By the addition of the second monolayer additional functionality can be achieved either by new symmetries, particle properties or a combination of both. For example colloids with significantly smaller particle sizes can be deposited to give complex AB_x structures as demonstrated by Fernández-Rodríguez using the Langmuir-trough technique.⁴¹

In this work, we elucidate the driving forces for the formation of 2D honeycomb and Moiré lattices of hard core/soft shell colloids. For the preparation of the ordered superstructures, we use a double deposition approach where two hexagonally ordered particle monolayers are assembled and transferred successively onto the same substrate. To do so we use the spontaneous self-assembly at air/water interfaces as the first and transfer from the interface to solid substrates as the second step. The final superstructure created by the two hexagonal monolayers can be controlled by the applied drying conditions. Slow drying leads to 2D honeycomb assemblies whereas fast drying results in 2D Moiré structures. Brownian dynamics simulations are used to explain the experimental findings and the resulting 2D assemblies. In particular, our study confirms that different structures (Moiré or honeycomb) are the sole consequence of different equilibration times rather than capillary forces, which are strong enough to deform the polymer shell.

Experimental section

Chemicals and materials

Gold(III) chloride trihydrate (Sigma-Aldrich, $\geq 99.9\%$), sodium citrate dihydrate (Sigma-Aldrich, $\geq 99\%$), butenylamine hydrochloride (Sigma-Aldrich, 97%), sodium dodecyl sulfate (Merck), *N*-isopropylacrylamide (NIPAM; Sigma-Aldrich, 97%), *N,N'*-methylenebisacrylamide (BIS; Sigma-Aldrich, 99%), potassium peroxydisulfate (Fluka, $\geq 99\%$), silver nitrate (99.999%, Sigma), ascorbic acid (p.a., Roth), acetonitrile (HPLC grade, Fisher Chemicals), ethanol (p.a., Honeywell) and Hellmanex III (Hellma GmbH) were used as received. Purified water (MQ-water) from a Milli-Q system (Millipore) with a final resistivity of 18.2 M Ω cm was used for all synthesis, purification and assembly steps. Microscope glass slides of 1 mm thickness (Menzel-Gläser, Thermo Scientific) were cut in pieces of approximately $1 \times 1 \text{ cm}^2$ and used as substrates for the particle assemblies.

Synthesis of core/shell microgels

The core/shell particles were synthesised in three steps, which are all easy to scale up in order to produce large quantities. First gold nanoparticles were synthesised according to the well-established Turkevich method.⁴² In the second step, these rigid nanoparticles were encapsulated in a cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) shell by seeded precipitation polymerisation following a well-established protocol.⁴³ The polymerisation was performed with a monomer concentration $c(\text{NIPAM}) = 0.06 \text{ M}$ and a nominal cross-linker (BIS) concentration of 15% with respect to the monomer NIPAM. After these steps core/shell particles with spherical cores of approximately 14 nm in diameter and hydrogel shells with an overall hydrodynamic diameter of 347 nm (20 °C, swollen state) were obtained. In a third step the cores of these core/shell particles were overgrown with silver (Ag). In order to obtain Ag–PNIPAM particles with 100 nm silver cores, a previously published protocol by Volk *et al.* was used.⁴⁴ Therefore, an ice-cold mixture of 2.65 mL MQ water and 0.5 mL acetonitrile was prepared in a round-bottom-flask. Then 79 μL of the core/shell particles (2 wt%), 2 mL of an ice-cold, aqueous ascorbic acid solution (49 mM) and 5.05 mL of a silver nitrate solution (15 mM) were added under stirring one after another. The reaction was allowed to proceed for 30 minutes before warming up to room temperature. The resulting particles were separated from dispersion by centrifugation at 2400 rcf for 25 min until the supernatant was completely colourless. After removal of the supernatant, the particles were redispersed in ethanol. This process was repeated three times for purification purposes. The concentration of the purified particles was determined gravimetrically and adjusted to approximately 1 wt%.

Interface-assisted assembly and double deposition

First, glass substrates were cleaned by sonication for 15 min in an aqueous Hellmanex solution (2 vol%). After that the substrates were rinsed with and further sonicated in water. Finally sonication in ethanol for 15 min was applied. After rinsing with ethanol, the substrates were dried with compressed, dry nitrogen. The core/shell particles were assembled at the air/water interface by dispensing a particle dispersion onto the water surface. Therefore, a crystallising dish (6 cm in diameter) was filled with MQ water and approximately 7 μL of a 1 wt% particle dispersion in ethanol was applied using an Eppendorf pipette. The freely floating particle monolayers were transferred onto 1 cm^2 glass substrates by careful immersion of the substrate below the particle monolayer and slow retraction at a 45° angle through the floating particle monolayer. The centre-to-centre distance was adjusted by the dwell-time of the monolayer at the air/water interface following the kinetics reported by us previously.¹⁴ The coated glass substrates were then carefully dried by blowing with a heatgun against the back of the substrate. For this a Steinel HL 1920E heatgun with a tunable temperature control between 80°C and 600°C (continuously variable with steps 1–9) was employed. The temperature was set to 7 and the fan to stage 3 ($300\text{--}500\text{ L min}^{-1}$). The sample was placed directly at the nozzle of the heatgun to avoid turbulences on the substrate. After approximately 10 s, the entire monolayer was dry including the accumulated water at the lower edge of the substrate. The main area of the monolayer was already dry after 3–5 s. Honeycomb and Moiré arrays were prepared by sequential deposition of two hexagonal particle monolayers onto the same substrate. For the application of the second monolayer, the substrate that was already coated once was treated with a heatgun for 10 s and with O_2 plasma for 15 s just before use. These steps were found to be crucial to attach the particles more firmly to the substrate and to enhance the hydrophilicity of the substrate. Then the substrate was immersed vertically into a crystallising dish which was filled with fresh MQ water. For this the substrate was clamped between self-looking tweezers and hung on a stand arm. Next a fresh particle monolayer was prepared at the air/water interface using the same method as above while the substrate was completely immersed in the aqueous phase. Slow, vertical retraction (90° with respect to the air/water interface) of the substrate by hand (approximately 10 s) through the particle monolayer lead to the deposition of the second monolayer. To obtain honeycomb structures, the withdrawn sample was left to dry slowly under ambient conditions. It took 5 minutes for the monolayer to dry and 10 minutes until also the lower edge had dried completely. For Moiré structures fast drying using a heatgun with the same settings as above (10 s) was employed.

Atomic force microscopy

1024×1024 pixel² topographic AFM images ($10 \times 10 \mu\text{m}^2$) were recorded with a Nanowizard 4 (JPK Instruments) in intermittent contact mode against air. OTESPA-R3 AFM probes (Bruker) were employed for imaging. The cantilevers had a nominal resonance frequency of 300 kHz and a spring constant of 26 N m^{-1} . The tip geometry was as visible apex with a nominal tip radius of 7 nm. The recorded height images were tilt-corrected using a polynomial line fit in the JPK SPM Data Processing software. The freely available ImageJ software was used to transform the color image into gray scale and thereof determine the centre of each particle in xy -coordinates. This information was then used to determine the centre-to-centre distance d_{c-c} and radial distribution function (RDF) of the particle monolayer.

Transmission electron microscopy

A Zeiss CEM902 transmission electron microscope with 80 kV acceleration voltage operated in bright-field mode was used to characterize the core/shell particles in terms of size and morphology. The sample was prepared on a carbon coated copper grid by applying a diluted droplet of the purified particle dispersion onto the grid. It was left to dry under ambient conditions. Image analysis was performed using the software ImageJ.

Brownian dynamics simulation

To gain more quantitative insights into the experimentally observed Moiré and honeycomb structures, we perform BD simulations. We use a square-shoulder potential^{45–49} to model these core/shell microgel particles using a hard core diameter σ surrounded by a soft shell with a total diameter $\lambda\sigma$ as illustrated in Fig. 1a. Thus, λ indicates the ratio between the outer soft shell and the inner hard core diameter. Following the work of Schoberth *et al.*,⁵⁰ we write the square-shoulder potential as

$$u(r) = \begin{cases} u_c(r) + u_f(r) & r < 1 + w \\ u_f(r) & 1 + w \leq r \end{cases} \quad (1)$$

with

$$u_f(r) = \frac{\varepsilon}{2} \left(1 + \tanh \left(\frac{\lambda - r}{w} \right) \right) \quad (2)$$

for the flat shoulder, and

$$u_c(r) = h\varepsilon \left(\frac{r - 1}{w} - 1 \right)^4 \quad (3)$$

for the hard core, where ϵ corresponds to the pair interaction energy, w denotes the width of the potential at the shell–shell contact, and h is the shoulder height. We consider $\lambda = 3.44$, which indicates the ratio of the soft shell diameter and the core diameter of a microgel particle in experiments. For simplicity, we set $w = 0.03$ and $h = 0.543$. The choice of w and h was to ensure the potential has a smooth gradient at the outer shell, and a strong repulsive force at the inner core. For parameters in the same range, the results do not change qualitatively. In fact, the actual values for w and h , however, do not possess any direct physical significance. A sketch of the potential $u(r)$ is shown in Fig. 1b. One observes a flat shoulder between distance σ and $\lambda\sigma$, where the particles do not feel any forces. Within our model, we can estimate a critical force barrier ($F_{\text{crit}} = 7k_B T/\sigma$) for the shell–shell overlapping, see the inset in Fig. 1b.

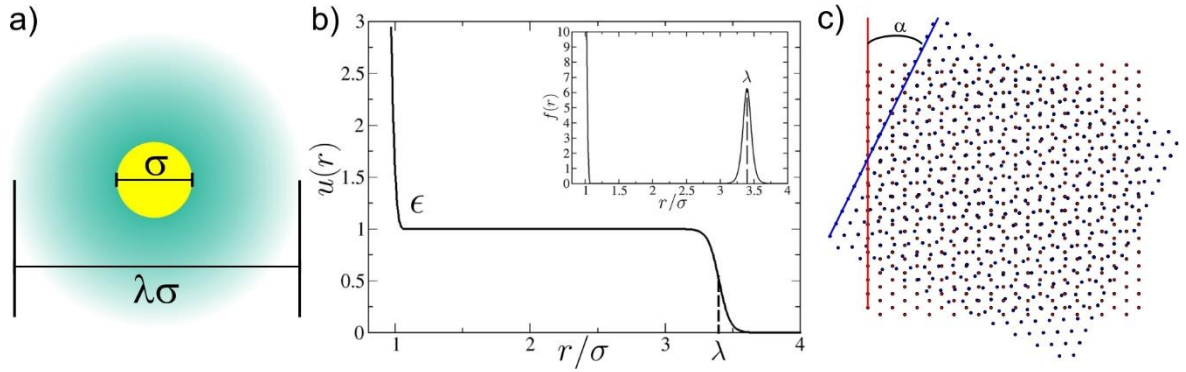


Figure 1. (a) Schematic representation of the core/shell microgel particles. (b) Square-shoulder potential having two characteristic length scales, namely, the hard core diameter σ and the total core/shell diameter $\lambda\sigma$. Inset: The radial part of the force $f(r)$ derived from $u(r)$. The dashed line illustrates the force at the shell–shell contact. (c) A typical illustration of rotation angle $\alpha = 30^\circ$ between two hexagonal layers.

Fig. 1c shows a schematic illustration of a bilayer system, where the bottom hexagonal layer is always fixed. Another hexagonal monolayer at a given rotation angle $\alpha = 30^\circ$ is positioned above the bottom layer, see also Fig. 3f for side-view. Next, to mimic the drying process of the experiments, a constant force F_{ext} (towards the negative z direction) is applied to the top hexagonal layer. Accordingly, particle positions $\vec{r}_i$ of the top layer evolve as

$$\dot{\vec{r}}_i(t) = \frac{D_0}{k_B T} [-\nabla_i u(r) + F_{\text{ext}}] + \sqrt{2D_0} R_i(t) \quad (4)$$

where D_0 denotes the short-time diffusion coefficient and $R_i(t)$ is Gaussian white noise with zero mean and unit variance:

$$\langle R_i(t) R_j(t') \rangle = \delta_{ij} \delta(t - t') \quad (5)$$

To obtain a straightforward comparison with experiments, we have used $\lambda\sigma = 347$ nm and $D_0 = 1.2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.⁵¹ We have further set $\varepsilon = k_B T$ and $t_0 = \lambda^2 \sigma^2 / D_0 = 0.1$ s respectively, as the units of energy scale and time scale. The equation of motion has been integrated with a finite time step $dt = 10^{-4} t_0$ using the Euler method, see ref. 52. Periodic boundary conditions are used in both x and y directions. Each simulation is performed up to 5 million time steps, which is equivalent to a total simulation time $t = 60$ seconds, in a box of size $L_x = 200\lambda\sigma$, $L_y = 200\lambda\sigma$, and $L_z = 2.5\lambda\sigma$.

Depending on the strength of the external force, one can observe interesting behaviours. For example, the soft shells do not overlap subjected to a small external force ($F_{\text{ext}} < 7k_B T/\sigma$), whereas for a large external force ($F_{\text{ext}} \gg 7k_B T/\sigma$) the soft shells entirely overlap and the core repulsion dominates. At an intermediate external force, the soft shells can overlap partially.

Results & discussion

Structure of colloids in dispersion and adsorbed on solid substrates

In this work core/shell colloids with silver nanoparticle cores and soft hydrogel shells based on chemically cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) were self-assembled into periodic 2D arrays. Fig. 2a shows a representative bright-field transmission electron microscopy (TEM) image of the colloids. The nearly spherical silver cores can be nicely distinguished from the hydrogel shells that are visible as grey corona around the cores due to the different electron densities. The mean diameter of the cores determined from several TEM images is $d_{\text{core}} = 101 \pm 10$ nm. The slight deviation from a perfect spherical shape is mainly attributed to the multicrystalline nature of the employed seed particles. The various crystal facets determine the overgrowth. This together with the polydispersity of about 10% leads to a slight broadening of the LSPR of the plasmonic particles and less pronounced quadrupolar mode as compared to the perfectly spherical and monodisperse particles.⁴⁴ The core quality however, does not impact the quality of the assembly since this is determined by the hydrogel shell. Related to the high vacuum in the TEM chamber, the hydrogel shells are imaged in their dry state and are therefore almost fully collapsed. Consequently, the shells appear much thinner than in the dispersed state, which is the relevant situation during particle assembly. The overall particle dimensions in dilute aqueous dispersion were determined by dynamic light scattering (DLS) in dependence of the dispersion temperature (Fig. 2b). Due to the volume phase transition (VPT) of the PNIPAM shell, a continuous decrease of the overall hydrodynamic diameter with increasing temperature is observed in the vicinity of the VPT temperature. This change in overall size is related to the shrinkage of the hydrogel shell upon release of water at poor solvent conditions.^{53–56} In the fully swollen state, we determine $d_h(\text{swollen}) = 347 \pm 2$ nm

(average for data of 15–19 °C), while the fully collapsed state yields $d_h(\text{collapsed}) = 228 \pm 1$ nm (average for data of 51–55 °C). Taking into account the diameter of the non-responsive cores, this implies a decrease of the shell thickness by almost a factor of two (from 123 to 64 nm). The VPT temperature is approximately at 34 °C as determined from the point of inflection of the deswelling curve. Using the core dimensions and the total hydrodynamic diameter d_h we calculate shell-to-core ratios $\lambda = d_h/d_{\text{core}}$ of 3.44 for the fully swollen state and 2.26 for the fully collapsed state. The core/shell particles were used for self-assembly at the air/water interface where freely-floating highly periodic monolayers are formed spontaneously.¹⁴ This spontaneous self-assembly is the result of attractive capillary interactions that occur due to local deformations of the air/water interface by the adsorbed core/shell microgels.^{57,58} The initial centre-to-centre distance of this monolayer is mainly determined by the hydrodynamic diameter of the core/shell particles. With increasing dwell-time at the air/water interface, the hydrogel shells slowly stretch out laterally driven by interfacial tension.⁵⁹ In consequence a continuous increase in the centre-to-centre distance occurs. Knowing the kinetics of this process from a previous study allows us to choose a certain centre-to-centre distance for the monolayer deposition onto the substrate.¹⁴ Fig. 2c shows an AFM height profile recorded from such a monolayer upon transfer on a solid substrate. Because the image was recorded in the dry state of the monolayer against air, the hydrogel shells are in a collapsed state resulting in the non-close packed appearance of the monolayer. Despite this drying of the shells, the particles are arranged in a hexagonal lattice with a nearest neighbour centre-to-centre distance of $d_{c-c} = 485 \pm 23$ nm. When the particles are transferred to the substrate they still possess their swollen and deformed dimensions but once the polymer is dried the remaining particle footprint on the substrate becomes much smaller. It has been shown that dry core/shell particles then adapt a fried-egg like morphology on the substrate.⁶⁰ The resulting spacing in between the particles is clearly visible in the cross-sectional traces in Fig. 2d. The average particle diameter in this dry state is $d_{\text{dry}} = 330$ nm. The void in a triplet of neighbouring particles in the hexagonal monolayer can accommodate a sphere with a diameter d_{void} according to:

$$d_{\text{void}} = \frac{2}{\sqrt{3}} d_{c-c} - d_{\text{dry}} \quad (6)$$

Details on the derivation of eqn (6) and a schematic depiction illustrating the void space can be found in Fig. S1 (ESI†). Using the experimentally determined values for d_{dry} and d_{c-c} one can calculate $d_{\text{void}} = 230$ nm. This value is much smaller than the hydrodynamic diameter in bulk (swollen state) and also significantly smaller than the dry state diameter d_{dry} . Thus, only colloids

that have a pronounced softness and that can undergo large deformation can penetrate into this void space.

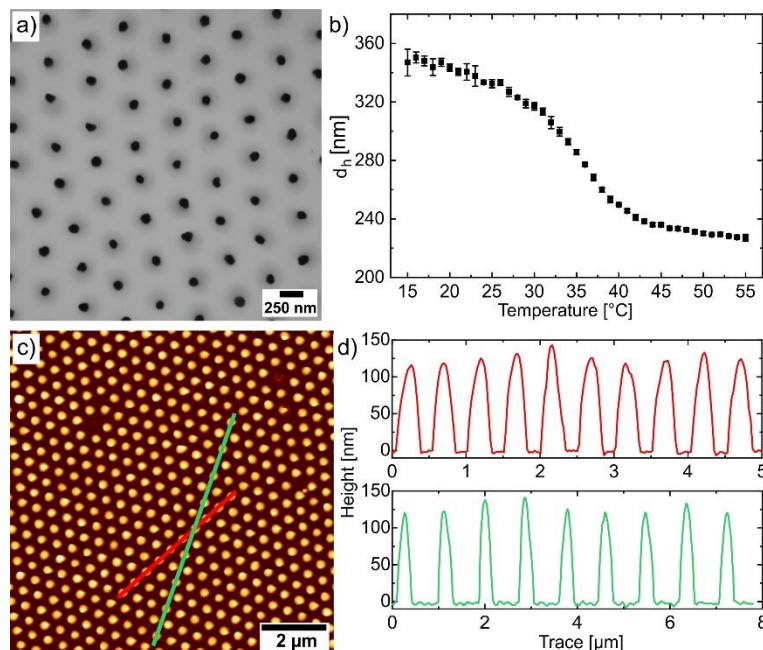


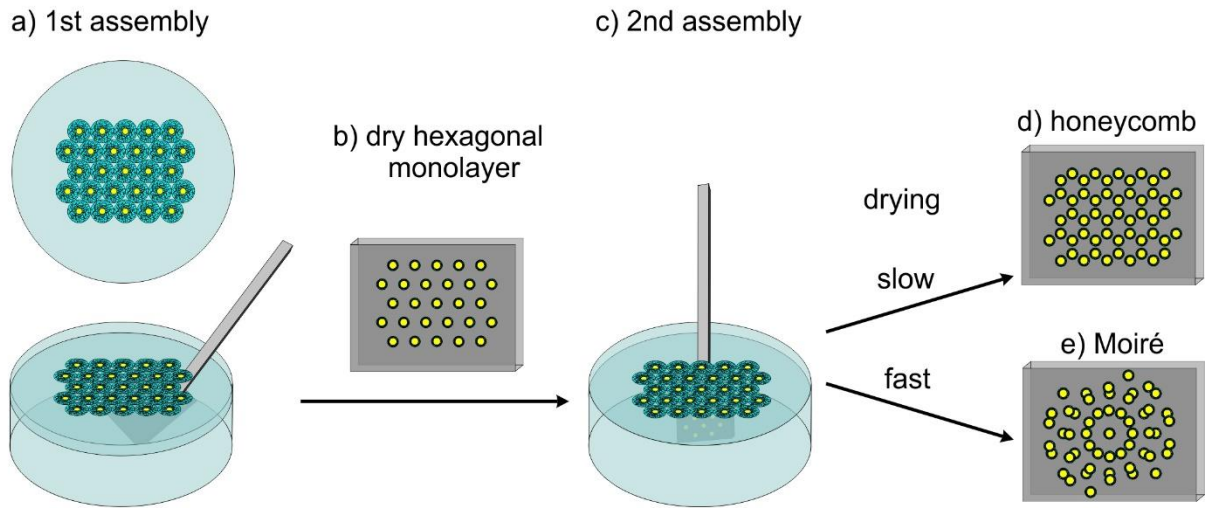
Figure 2. Characterisation of the hard core/soft shell Ag-PNIPAM particles. (a) Bright-field TEM image showing the particles in the dry state. (b) Evolution of the hydrodynamic diameter d_h with temperature in aqueous dispersion. The VPT temperature is at approximately 34 °C. (c) AFM image of a hexagonally ordered particle monolayer with $d_{c-c} = 485 \pm 23$ nm obtained from a single deposition step. (d) Cross-sections from AFM height images generated along the red and green lines in (c).

Assembly process and simulation conditions

Fig. 3 schematically depicts the two sequential self-assembly steps and the structures of the resulting monolayers. A first monolayer is prepared at the air/water interface and subsequently transferred onto a glass substrate by retracting the glass substrate through the monolayer at an angle of 45° (for details see Experimental section). Upon drying, the hydrogel shells collapse around the hard core resulting in a non-close packed, hexagonally ordered particle monolayer (see Fig. 2c and 3b). For the second monolayer deposition, the substrate coated with the first monolayer is submerged into water before depositing a fresh monolayer at the air/water interface above (Fig. 3c). Then the substrate is carefully withdrawn vertically through the second monolayer at the interface. The change in the retraction procedure has two reasons. First, the coated substrate needs to be submerged into the aqueous phase before the new monolayer is applied because otherwise particles would attach during the immersion process. Hanging the sample vertically was therefore the obvious choice. Secondly, we wanted to move/tilt the sample the least possible way during retraction and drying in order to achieve reproducible drying conditions for every prepared sample. After this second transfer step, two

different monolayer structures are observed depending on the drying conditions: when the second monolayer is dried slowly in the course of 5 minutes, honeycomb structures are formed (d). Rapid drying within 3–5 seconds on the other hand results in the formation of Moiré structures (e). The bottom row of Fig. 3 shows a schematic illustration of the Brownian dynamics (BD) simulation procedure is depicted in side-view.

Experimental preparation procedure



Simulation procedure

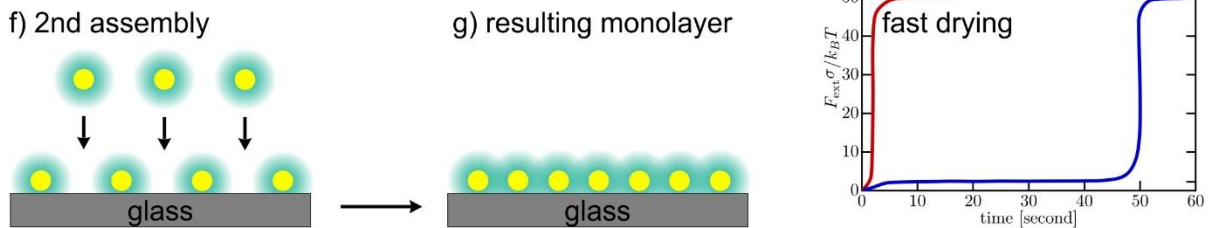


Figure 3. Top: Sketch of the self-assembly process for honeycomb and Moiré structures from left to right: (a) 1st assembly step: crystallising dish with hexagonally ordered, swollen core/shell colloids at the air/water interface (top view) and immersed glass substrate below monolayer (side view). (b) In the dried state, the monolayer features non-close packed hexagonal order due to shrinkage of the hydrogel shell (dry hexagonal monolayer). (c) 2nd assembly step: the coated substrate is immersed into water before the second monolayer is assembled and withdrawn onto the substrate carrying the first monolayer. (d) Slow drying of the particle array leads to the formation of honeycomb structures and fast drying to (e) Moiré structures. Bottom: Side view of the Brownian dynamics simulation protocol: (f) a particle layer (hexagonally ordered) is attached to the glass substrate and has no translational motion. Another hexagonal layer is placed above the bottom layer. A constant external force imposed on the top hexagonal layer squeezes these two layers into one monolayer (g). Two different protocols are presented to explain fast and slow drying processes in simulations (h).

A hexagonally ordered monolayer is immobilised on the solid substrate and a second monolayer is placed above the bottom layer (f). Then a constant external force is imposed onto the mobile

top layer. Consequently, the top layer is squeezed into the plane of the attached monolayer on the glass surface (g). Depending on the protocol used for the time-dependence of the external force, slow and fast drying can be mimicked and either honeycomb or Moiré structures are obtained, see Fig. 3h.

Comparison of microstructures from experiment and simulation

Fig. 4 shows the results from a second monolayer deposition on top of the first, hexagonally ordered monolayer depicted in Fig. 2c. In Fig. S2 (ESI†) the individual sublattices are highlighted in red and blue colour for easier illustration. For the sample with a honeycomb microstructure (Fig. 4a) slow drying conditions were applied whereas the Moiré structure in Fig. 4d is the result from fast drying using a heatgun. The honeycomb structure is visible over the whole AFM image and is only disrupted at domain boundaries. These occur due to the self-assembly process which inherently produces some point and line defects. Furthermore, the individual hexagonal sublattices are multidomain structures consisting of smaller single crystalline domains with different orientations. These characteristics also translate into the monolayers obtained from the double deposition process, *i.e.* also the honeycomb lattice is a multidomain sample. Analysis using fast Fourier transformation (FFT) of the real space particle positions nevertheless demonstrates the long range order of the honeycomb microstructure by the occurrence of multiple orders of Bragg peaks (Fig. 4b). Since the honeycomb structure is formed by the settlement of the particles of the second hexagonally ordered monolayer into the voids presented by three particles of the first monolayer,⁴⁰ the honeycomb structure is characterised by a hexagonal symmetry reflected by the six-fold symmetry of the Bragg peaks in the FFT. Taking into account the void space ($d_{\text{void}} = 230$ nm, eqn (6)), it becomes clear that the hydrogel shells undergo significant deformation in the honeycomb lattice. Now we compare the experimentally produced microstructure to the results from BD simulations depicted in Fig. 4c. Here a perfect honeycomb microstructure obtained by mimicking the slow drying process is shown. To compare the experimental and simulated structure, we calculate the radial distribution function (RDF) from xy -coordinates of the particle centre positions in the real space AFM images and structures obtained from BD simulations (inset in Fig. 4b). The RDF describes the average particle density around a central particle as a function of the radial distance^{58,61} and therefore can help to identify regular patterns. When an increase in particle density at a certain distance from a chosen centre particle is detected a peak in the RDF will occur. The RDF is an averaged response over all the particles in the monolayer. We can see a good match of the RDF traces from experiment (blue RDF) and simulated monolayer (yellow RDF) with only deviations in intensity and peak width. These deviations are explained by some degree of

positional disorder and the presence of domain boundaries in the experimental sample as compared to the perfect structure from simulation.

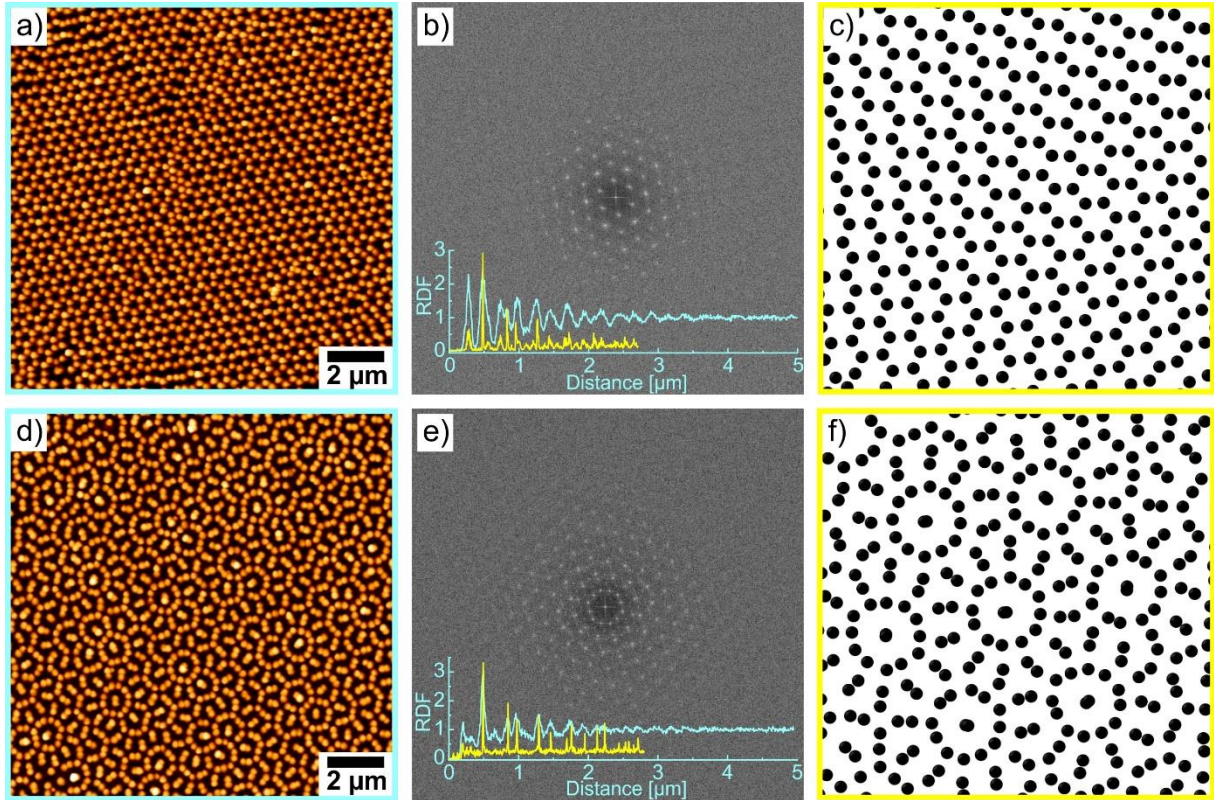


Figure 4. Comparison of the experimentally observed microstructures to results from theoretical simulation. (a) AFM height image of a honeycomb monolayer obtained by slow drying of the second monolayer on top of the first one. (b) FFT of experimental honeycomb structure and RDFs of experimental (blue trace) and calculated (yellow trace) honeycomb structure as inset. (c) Honeycomb microstructure as a result from BD simulations. (d) AFM height image of a Moiré monolayer prepared by fast drying of the second monolayer on top of the first monolayer. (e) FFT of experimental Moiré structure and RDFs of experimental (blue trace) and calculated (yellow trace) Moiré structure as inset. (f) Moiré microstructure as a result from BD simulations with $\alpha = 30^\circ$.

Next the same analysis is performed for the experimental Moiré structure depicted in Fig. 4d. The FFT (Fig. 4e) shows multiple orders of Bragg peaks again indicating a long range order. The 12-fold symmetry points to a rotational offset between the first and second deposited hexagonally ordered particle monolayer. This is confirmed by the matching structure obtained from BD simulations when a rotation angle $\alpha = 30^\circ$ is employed for structure formation (Fig. 4f). For closer comparison RDFs are given as insets in Fig. 4e. Again a good match of the traces is found with deviations in peak width and intensity due to the imperfect experimental microstructure. Since we use fast drying conditions the particles from the second deposition step cannot settle slowly into the voids presented by the firstly deposited monolayer but are pushed into the first lattice with the orientation they possess at the air/water interface in regard

to the monolayer attached to the glass. Consequently, the initial orientation of the two monolayers determines which Moiré motif is formed. Since we cannot control this orientation in experiment, samples with other Moiré motifs corresponding to different rotation angles between the first and the second layer were obtained. Some examples are shown in Fig. S3 (ESI†).

In order to show that our monolayers from the sequential double deposition are real 2D structures rather than an AB stacking of two monolayers as previously reported for example for hard spheres,⁶² we provide AFM cross-sections for the Moiré and honeycomb assemblies (Fig. 5a). The green cross-section profile corresponds to the hexagonal monolayer after the first deposition onto the solid substrate (see Fig. 2d) and is included for better comparison. The average maximum height of the particles in this monolayer is approximately 125 nm and all particles sit in the same plane on the substrate. The cross-sections in red and blue were measured from the honeycomb lattice (red) and the Moiré lattice (blue) along straight lines as illustrated in the AFM height images in Fig. 5b and c.

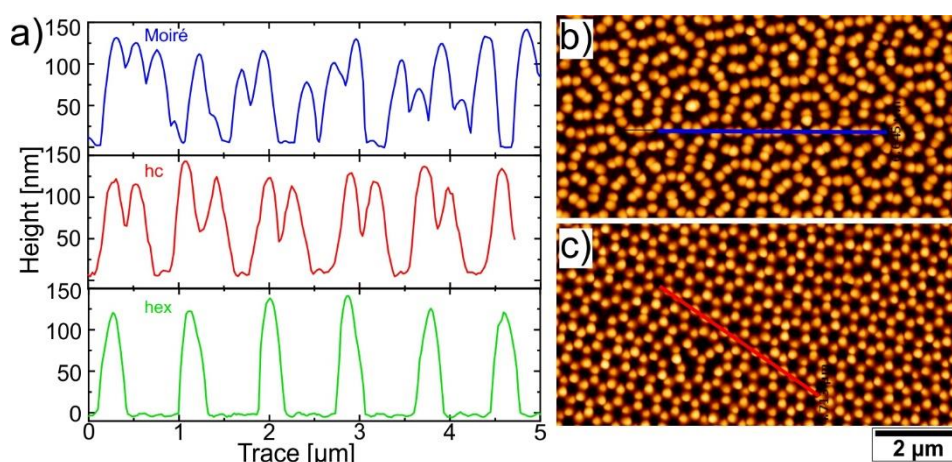


Figure 5. Cross-section analysis of different monolayers. (a) Experimental cross-sections for single hexagonal monolayer (green), honeycomb (hc) lattice (red) and Moiré lattice (blue). (b and c) Corresponding AFM height images with the traces (solid lines) used for the cross-section analysis in (a).

The average maximum height in the Moiré and honeycomb lattices are very similar to the ones determined for the single hexagonal monolayer and again all particles sit in the same plane on the substrate. This highlights that we indeed deal with real 2D structures, *i.e.* particle monolayers. Slight variations in particle height can be mainly attributed to the fact that the cross-section does not always go directly through the centre of the particles due to a particle arrangement that does not follow a straight line (particularly the Moiré pattern). Only when a particle from the first and second monolayer would settle in the same spot due to the given Moiré motif, the second particle sits on top of a particle of the first layer. Since the particle

cannot occupy the same place in the 2D lattice as the first particle, the 2D pattern is broken in this particular position (Fig. S4, ESI[†]).

Before we discuss the simulation results, we make a clear distinction between the fast and the slow drying process in simulations: a setup that is dried by rapid heating will experience a large external force ($F_{\text{ext}} = 50k_{\text{B}}T/\sigma$) within a couple of seconds, whereas in a slow drying process we let the system to equilibrate for 50 seconds and then apply a large external force ($F_{\text{ext}} = 50k_{\text{B}}T/\sigma$), see Fig. 3h.

During the drying process, the normal component of capillary forces (F_{cap}) is balanced by the frictional drag force and the repulsive forces (F_{rep}) originating from the bottom layer, leading to the following equation $F_{\text{cap}} = \gamma v + F_{\text{rep}}$ (7) where $\gamma = k_{\text{B}}T/D_0$ is the Stokes friction coefficient of each particle and v is the velocity of the drying front. From the experimental findings for v and D_0 , we calculate that the drag force (γv) is of the order of $1.0k_{\text{B}}T/\sigma$. Furthermore, we know that each particle requires about $7k_{\text{B}}T/\sigma$ for the shell-shell overlapping, see the inset of Fig. 1b. Since there are at least 4 neighboring particles, the total repulsive force should be about $F_{\text{rep}} \sim 28k_{\text{B}}T/\sigma$. Therefore, we chose the normal component of capillary forces $F_{\text{cap}} = 50k_{\text{B}}T/\sigma$ in our simulations to ensure the perfect penetration of the drying front into the bottom layer. As long as F_{ext} is larger than $30k_{\text{B}}T/\sigma$, the actual value does not matter as revealed by our simulations.

In order to study a Moiré structure formation, the highly packed (2D packing fraction = 0.9) top hexagonal layer rotated by an angle $\alpha = 30^\circ$ is placed above the highly packed bottom layer. Subsequent application of a large external force ($F_{\text{ext}} = 50k_{\text{B}}T/\sigma$) overcomes the force barrier required for the shell-shell overlapping, and eventually squeezes these two layers into one monolayer. This is equivalent to a fast drying process in experiments. Similar to experiments, the resulting monolayer shows a 12-fold symmetry (Moiré structure), in particular, one centre particle is surrounded by 12 particles at equal distance, see Fig. 4f. For clarity, we only plot the hard-core diameter of the microgel particles in Fig. 4. We also notice that there are two particles at the centre of each Moiré pattern, and one of them remains outside the 2D plane, which is also in line with experimental observations, see Fig. 4d and height trace in Fig. S4 of the ESI.[†] This is expected because two hard cores cannot overlap.

To realise the slow drying process, we use the previous bilayer configuration with a rotation angle of $\alpha = 30^\circ$, and then allow the system to equilibrate in the course of 50 seconds. During this equilibration process, we apply a small external force ($F_{\text{ext}} = 1k_{\text{B}}T/\sigma$) on the top layer so that particles from both layers can interact without overlapping. Interestingly, we observe a structural transition of the top layer particles due to the soft nature of the shells, in particular,

particles of the top layer rotate from 30° to 2° . This indicates that particles in the top layer try to adapt the configuration of the immobile bottom layer. In fact, this structural transition is valid for any starting rotation angle α . As an example, we present a structural transition from 13° to 2° in Fig. 6. At the end of this structural transition, we again apply a large external force ($F_{\text{ext}} = 50k_{\text{B}}T/\sigma$) to the top layer, and obtain honeycomb structures in the 2D plane with 6-fold symmetry, see Fig. 4a–c. Hence, a good agreement is found between experiments and simulations for different drying processes, which makes it possible to create mechanically stable honeycomb (slow drying) or Moiré (fast drying) structures in the 2D plane using a highly packed hexagonal bilayer system.

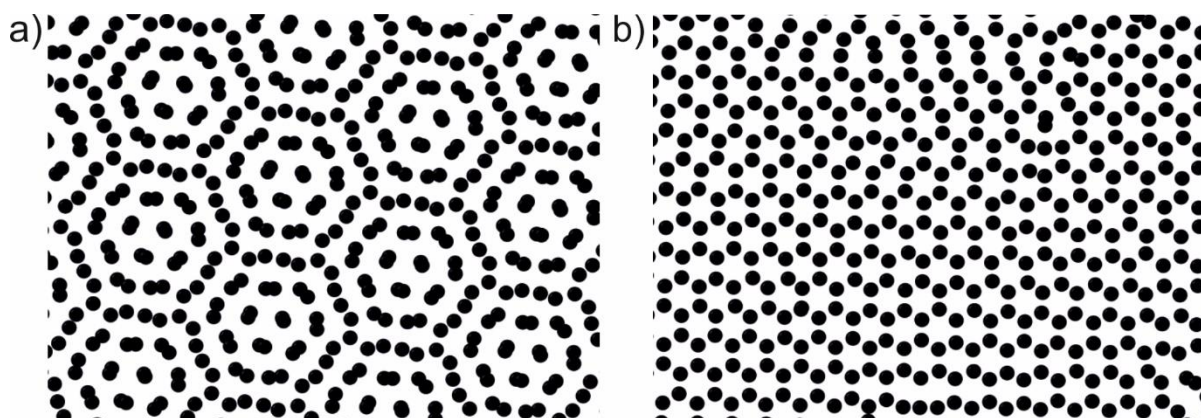


Figure 6. (a) Two highly packed hexagonal layers with rotation angle of 13° . For simplicity, we plot only the core diameters of the microgel particles. (b) The final configuration after an equilibration time of 50 seconds. The particles of the top layers rearrange from 13° to 2° .

To provide robustness of our protocol, we also increase the shoulder width from $\lambda = 1.3$ to $\lambda = 4$, and obtain similar results. However, for $\lambda < 1.1$, hard core interactions dominate, and therefore it is not possible to squeeze a highly packed (2D packing fraction = 0.9) hexagonal bilayer into a monolayer. This further highlights that particles with two length scales are necessary to form mechanically stable honeycomb or Moiré structures in the 2D plane.

Conclusions

Core/shell microgels with rigid cores and soft, deformable hydrogel shells spontaneously self-assemble at air/water interfaces due to attractive capillary interactions. The resulting freely floating monolayers are characterised by a hexagonal arrangement of the microgels with centre-to-centre distances that are governed by the thickness and swelling state of the hydrogel shells. Upon transfer onto a solid substrate – in our case glass – centimetre-scale, homogeneous coatings with large, single crystalline domains are obtained. Subsequent double deposition of monolayers onto the same substrate gives access to more complex 2-dimensional structures.

Slow drying of the second on top of the first monolayer yields honeycomb lattices. In contrast, fast drying reveals Moiré lattices. In the latter case the exact structure is determined by the rotation angle between the domains of the first and the second monolayer. Because of the multidomain character of the hexagonal sublattices, Moiré structures with various rotation angles are found on the same substrate. All observed lattices are real 2-dimensional monolayers which means that all particles settle into the same lattice plane. This is the result of significant shell deformation and evidenced by cross-sectional analysis using atomic force microscopy.

Brownian dynamics simulations of the double deposition process support our experimental findings. Most importantly the simulations show that the fast drying conditions in experiment lead to Moiré structures as a non-equilibrium deposition, that is, when the second layer is squeezed into the first layer at sufficiently large forces. Contrary, rearrangement of the particle in the second monolayer occurs under equilibrium conditions corresponding to slow drying in experiment, leading to honeycomb lattices.

The present work resembles an important step toward surface nanostructuring using soft colloids. In future it would be interesting to study assembly of soft anisotropic colloids.^{63–68}

Acknowledgements

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Supporting Information

Void space in single hexagonal monolayer

Figure S1 illustrates the void space in between three neighboring particles of a hexagonal monolayer with a center-to-center nearest neighbor distance d_{c-c} . The yellow circles illustrate the rigid cores of the core/shell particles with the green surrounding circles being representative of the soft, deformable hydrogel shells. In the dry state the core/shell particles have a diameter d_{dry} . The void can accommodate a spherical particle with a footprint diameter d_{void} .

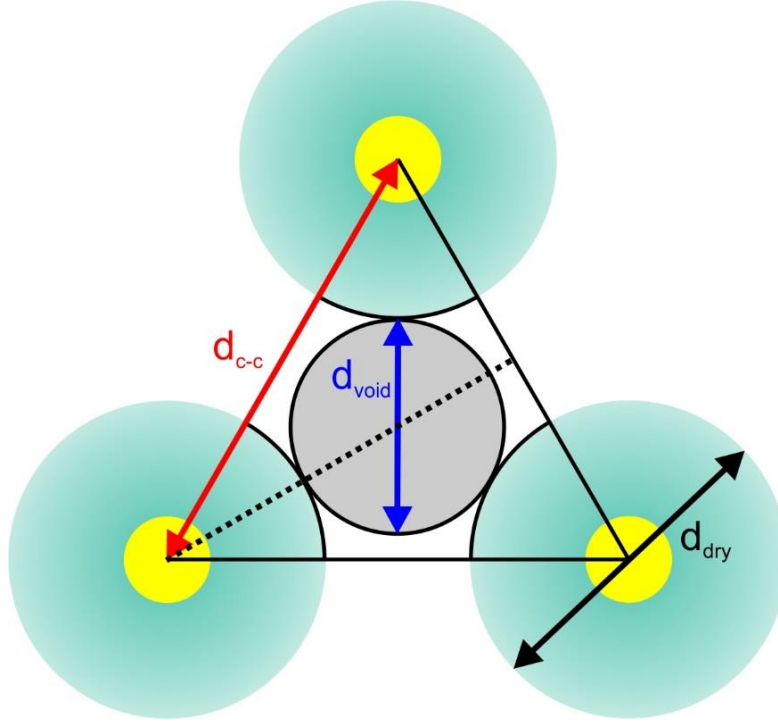


Figure S1. Schematic depiction of void space with the diameter d_{void} in the center of three dry core/shell particles with a diameter d_{dry} and a center-to-center distance of d_{c-c} .

The length l of the dashed line (altitude) in figure S1 is:

$$l = \frac{\sqrt{3}}{2} d_{c-c} \quad (S1)$$

The center of the gray circle divides l in a 2:1 ratio. Correspondingly the radius of the gray circle $r_{void} = \frac{1}{2} d_{dry}$ is $\frac{2}{3} l$ minus the dry core/shell particle radius $r_{dry} = \frac{1}{2} d_{dry}$. Thus:

$$r_{void} = \frac{2}{3} \frac{\sqrt{3}}{2} d_{c-c} - r_{dry} = \frac{1}{\sqrt{3}} d_{c-c} - r_{dry} \quad (S2)$$

The void diameter is then given by:

$$d_{\text{void}} = \frac{2}{\sqrt{3}} d_{c-c} - d_{\text{dry}} \quad (\text{S3})$$

Hexagonal sublattices in honeycomb and Moiré lattices

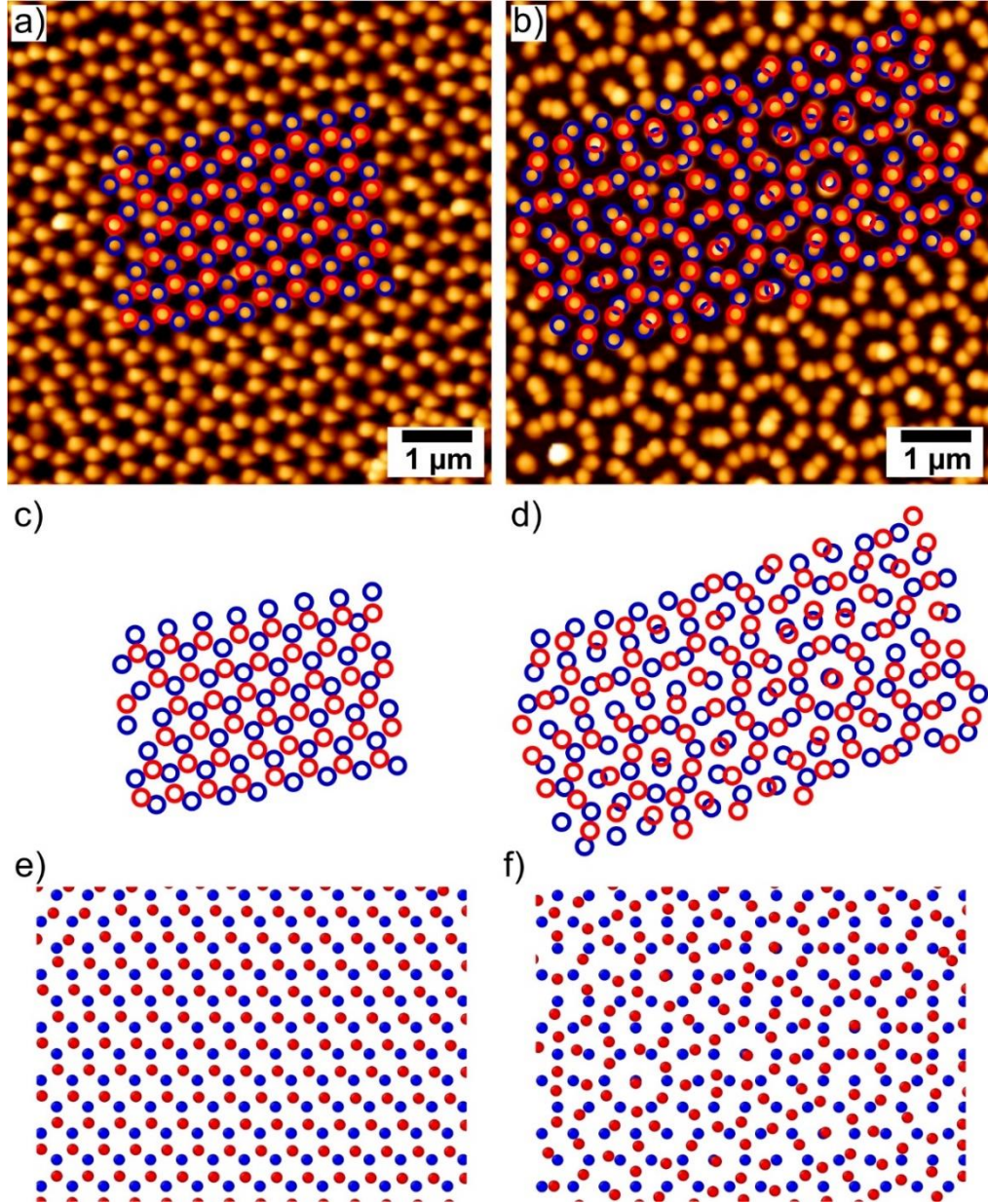


Figure S2. Visualization of the two hexagonal sublattices (blue and red circles) in AFM images of (a) the honeycomb microstructure and (b) the Moiré lattice. In (c) and (d) the indicated sublattices are shown without the underlying AFM image for better visibility. (e) and (f) show the two sublattices from BD simulations.

Influence of rotation angle on Moiré lattices

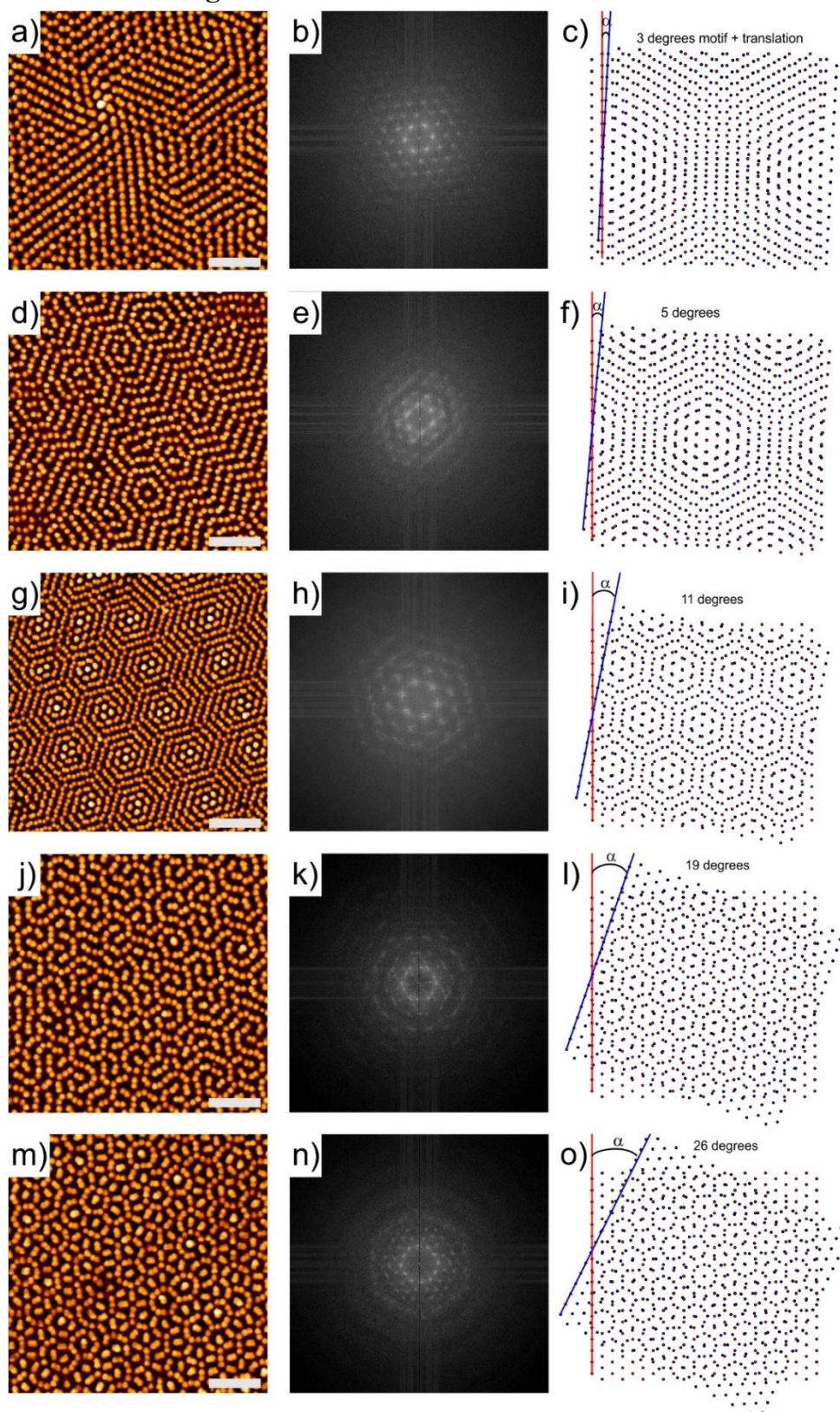


Figure S3. Characterization of different Moiré motifs: AFM height images (a, c, g, j, m) and respective FFTs (b, e, h, k, n) and sketches of two overlaid perfect hexagonal patterns with angle of rotation α matching the experiment to give Moiré motifs (c, f, i, l, o).

Cross-section analysis of Moiré lattices

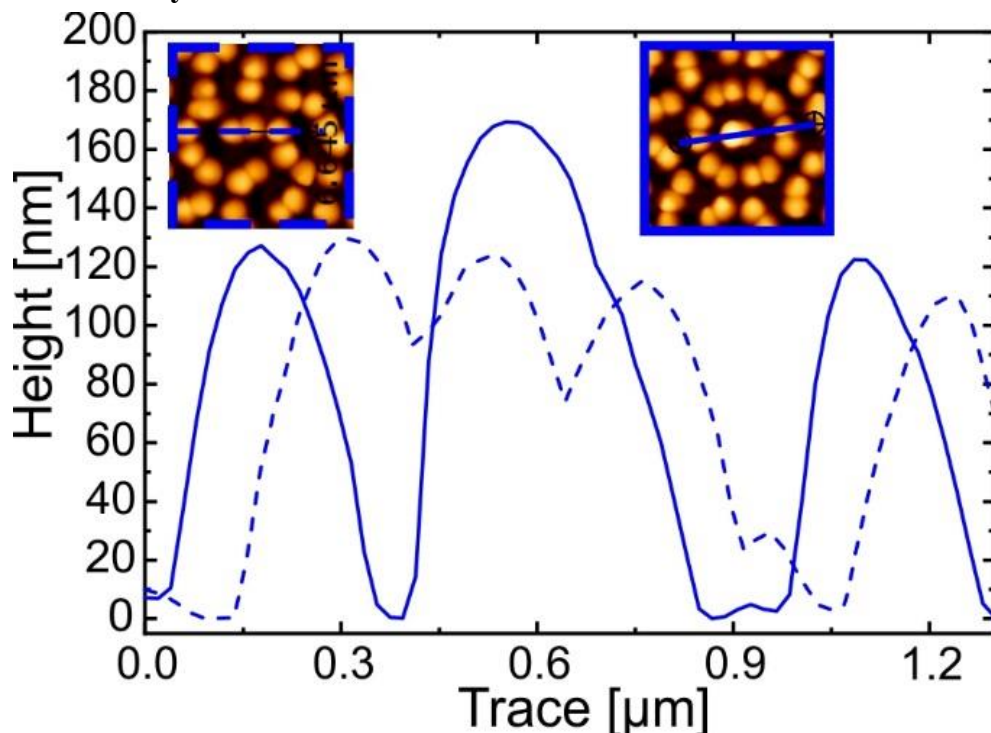


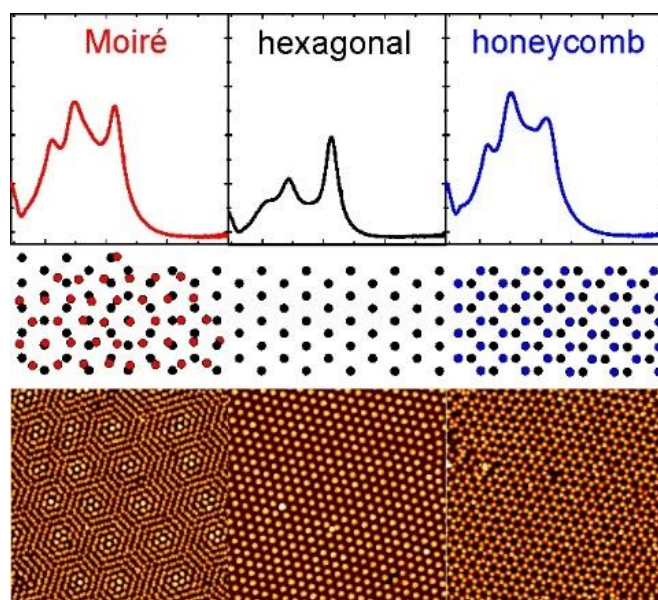
Figure S4: Cross-section analysis of an experimental Moiré structure along different trajectories. For the dashed line all particles sit next to each other in a single plane. The solid line cross-section crosses a position where two particles are deposited on nearly the same spot and thus the particle from the second deposited layer sits on top of the underlying particle from the first monolayer. In the latter case the upper particle is sterically hindered to settle into the underlying monolayer plane. Thus the cross-section shows a significantly increased total height at this particular position. Insets depict the corresponding AFM height images with the traces used for the cross-sections.

8 Surface Lattice Resonances in Self-Templated Plasmonic Honeycomb and Moiré Lattices

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Keywords: core-shell colloids, honeycomb lattices, Moiré lattices, self-assembly, surface lattice resonances



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Abstract

Surface lattice resonances appear in periodic plasmonic nanoparticle arrays due to the hybridization of plasmonic and photonic modes. Compared to localized surface plasmon resonances of single particles, these coupled modes feature reduced linewidth, angle-dependent dispersion, and long-range collectivity. Here, the optical response of self-assembled plasmonic monolayers of periodically arranged gold and silver nanoparticles is studied. In comparison to already established hexagonal lattices, self-templated honeycomb and Moiré type lattices as well as their binary counterparts that include silver and gold nanoparticles in the same monolayer are looked at. All periodic arrays feature macroscopic dimensions (cm-scale) and support surface lattice resonances as evidenced from classical extinction measurements. The experimental findings are supported by results from finite difference time domain simulations. Variation of the plasmonic material, the lattice spacing, and geometry enables spectral tunability of the optical response of the lattices.

Introduction

Self-assembly of plasmonic colloids enables the fabrication of functional materials with optical responses that can capitalize on plasmon resonance coupling phenomena.¹⁻⁴ In recent years researchers have mostly focused on controlling small inter-particle spacings on the order of a few to a few tens of nm where effects related to the strong near-field close to the surface of plasmonic nanoparticles are relevant.^{2, 5-10} In contrast, periodic arrays of plasmonic nanoparticles with wavelength scale periodicities are able to support surface lattice resonances (SLRs).¹¹⁻¹⁵ SLRs are collective, coupled modes between the localized surface plasmon resonance (LSPR) of the single nanoparticles (NPs) and the diffractive modes of the lattice.¹² The coupling strength and the SLR position depend on the LSPR properties of the individual plasmonic nanoparticles and the position of the Bragg modes, typically with the Bragg modes at slightly larger wavelength than the LSPR maximum.^{11-13, 16-17} This implies that not only control over the nanoparticle size, responsible for the LSPR position and strength, but also on lattice periodicity, responsible for the spectral position of the Bragg modes, is required. Furthermore, it has been shown that the refractive index (RI) environment is crucial for strong coupling between plasmonic modes and in-plane modes of diffraction.^{12-13, 18-21} The narrow linewidth of SLRs, implying long lifetimes, and their precise tunability by the lattice period,^{19, 22-24} plasmonic material,²⁵ particle shape²⁶⁻²⁷ and the effective refractive index of the surrounding environment^{18-19, 23, 28} is of high relevance to several nanooptical applications like sensing,²⁹⁻³⁰ energy-transfer processes³¹⁻³² and lasing.³³⁻³⁶ In the last decade works addressing SLRs in periodic plasmonic lattices mostly rely on samples that were prepared lithographically,

e.g. by electron³⁷ and soft interference lithography.²⁶ The dominating structures were square as well as hexagonal lattices. Since lithographic fabrication approaches rely on masks and etching processes that can be altered at will, despite limitations through the resolution, other array structures become available. The existence of SLRs in honeycomb structures was first shown by Humphrey and Barnes in 2014.³⁷ The authors compared the optical response of square, hexagonal and honeycomb arrays and found similar SLRs independent of the array structure. Furthermore, Guo *et al.* elucidated the geometry dependence of SLRs, precisely for square, rectangular, hexagonal, honeycomb and Lieb lattices.³⁸ It was shown that SLRs present in honeycomb lattices follow the same diffractive orders as for hexagonal lattices and that only the intensity of the extinction is increased due to an increased number of particles in the lattice. In contrast to the top-down fabrication by lithography, a colloid based approach strongly benefits from the fact that plasmonic nanoparticles can be prepared with a wide range of shapes and sizes allowing to tailor the LSPR strength and position. Furthermore, wet-chemical synthesis yields typically crystalline or even single crystalline plasmonic nanoparticles. Crystalline plasmonic nanostructures are expected to have longer dephasing times³⁹ and thus superior plasmonic properties.⁴⁰ Losses due to scattering at grain boundaries and lattice defects in amorphous/poorly crystalline plasmonic nanostructures can broaden the LSPR and reduce its intensity.⁴¹ In a previous study we have shown that the encapsulation of wet-chemically synthesized, crystalline plasmonic particles in soft, deformable hydrogel shells can be used to achieve control over the inter-particle distance in particle monolayers.⁴² In order to fabricate periodic plasmonic lattices from colloidal building blocks, self-assembly is an ideal bottom-up tool that is efficient and typically low-cost. Inherently, self-assembly of spherical particles leads to the formation of hexagonal superstructures and a lot of effort is put into the preparation of more complex structures.^{24, 43-46} Particularly interesting is the self-assembly at liquid/liquid or air/liquid interfaces because of its experimental simplicity and the high degrees of order it can produce.⁴⁷ We have recently shown that the assembly of core-shell microgels at air/water interfaces is ideally suited to prepare periodic, plasmonic monolayers where the plasmonic properties can be tailored by the choice of the metal cores.^{17, 48} Further, self-assembly generally allows for the combination of different plasmonic materials, for example, to produce binary plasmonic lattices of gold and silver nanoparticles.⁴⁹ Gold and silver nanoparticles of the same size and shape feature LSPRs at different spectral positions with stronger resonances in case of silver due to lower losses as compared to gold that shows high intrinsic absorption losses in the visible wavelength range.^{41, 50} It has recently been demonstrated that the assembly of heterogeneous superstructures that feature different nanoparticles and/or various inter-particle

spacings presents an interesting concept to reduce plasmonic losses.⁵¹ While the influence of size heterogeneity has been studied in periodic lattices of plasmonic dimers consisting of silver disks with different sizes,⁵² the influence of material heterogeneity has not been addressed so far. To the best of our knowledge the optical response of binary plasmonic lattices with wavelength scale periodicities have not been studied, yet.

In this work, we study the optical response of self-assembled silver, gold and binary gold/silver nanoparticle honeycomb and Moiré type lattices in direct comparison to already established hexagonal lattices. All lattices were prepared from core-shell microgels with plasmonic gold and silver nanocrystal cores, that were self-assembled at the air/water interface and subsequently transferred to glass substrates. Following a recently published protocol we used the self-templating of hexagonal lattices onto the same substrate to fabricate the honeycomb and Moiré type superstructures.⁵³ We investigated the optical properties of the lattices experimentally by UV-Vis absorbance spectroscopy and theoretically by finite difference time domain (FDTD) simulations. SLRs were observed for all lattices. The strength and position of the SLRs strongly depend on the lattice constant and the degree of order.

Results and Discussion

Plasmonic Core-Shell Building Blocks

In this work we used core-shell microgels with plasmonic metal cores and soft, cross-linked poly-*N*-isopropylacrylamide (PNIPAM) hydrogel shells as building blocks for the preparation of periodic nanoparticle arrays.⁵⁴ The core-shell particles were synthesized by seeded precipitation polymerization⁵⁵ followed by subsequent overgrowth of the initial gold cores. The overgrowth of these cores by silver and gold was performed following protocols recently published by Volk *et al.*¹⁸ and Honold *et al.*,⁴⁸ respectively. In the following, the particles will be referred to as Au-PNIPAM and Ag-PNIPAM. Figure 1a,b shows representative transmission electron microscopy (TEM) images of the particles containing silver cores with an average diameter of $d_{\text{Ag}} = 101 \pm 10$ nm (a) and gold cores with an average diameter of $d_{\text{Au}} = 100 \pm 8$ nm (b). The dry polymer shell surrounding each particle is visible as grey corona against the background. Histograms of the core size distribution and additional TEM images of both particle types can be found in Figure S1, Supporting Information.

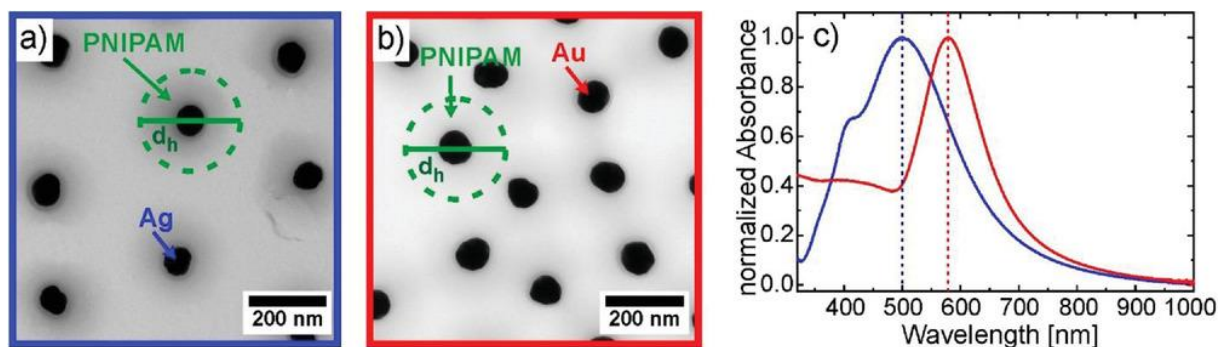


Figure 1. Characterization of the core-shell colloids: TEM images of a) Ag-PNIPAM and b) Au-PNIPAM particles. The green, dashed circles indicate the swollen-state hydrodynamic diameter, d_h , in aqueous dispersion. c) Normalized UV-vis absorbance spectra of dilute, aqueous particle dispersions (blue trace: Ag-PNIPAM; red trace: Au-PNIPAM). The vertical dashed lines highlight the wavelengths of the dipolar LSPR maxima.

Hydrodynamic diameters of $d_h = 336$ nm were determined for both types of particles by dynamic light scattering (DLS) measured from dilute aqueous dispersions at 20 °C. This overall, swollen-state particle dimension is highlighted in the TEM images of Figure 1a,b as green dashed circles. The plasmonic properties of the core-shell particles were studied by UV-vis absorbance spectroscopy using dilute particle dispersions in water. Due to the low concentration (<0.05 wt%) inter-particle distances are large and electromagnetic coupling can be excluded. The spectra shown in Figure 1c reveal dipolar localized surface plasmon resonances (LSPRs) for the Ag-PNIPAM particles (blue trace) with a maximum at 500 nm (blue, vertical dashed line) and for the Au-PNIPAM (red trace) at 578 nm (red, vertical dashed line). For Ag-PNIPAM an additional shoulder at 413 nm is visible. This additional resonance is attributed to a weak quadrupolar LSPR contribution typical for large enough silver nanoparticles.⁵⁶ This was previously also reported by us and theoretically supported through Mie theory calculations.⁴⁸

Both types of core-shell particles were used to prepare periodic, plasmonic lattices using colloidal self-assembly at air/water interfaces.⁴⁸ The assembly process for the formation of the self-templated honeycomb (hc) and Moiré lattices starting from hexagonally ordered arrays was recently reported by us.^{49,53} A detailed description of the assembly procedure and the sample characterization can be found in the Supporting Information.

Characterization of the Plasmonic Monolayers

The atomic force microscopy (AFM) height image of the first, deposited monolayer displayed in Figure 2a reveals a regular hexagonal pattern formed by the core-shell particles. Image analysis using fast Fourier transformation (FFT) showed pronounced Bragg peaks of several orders with a sixfold symmetry. Furthermore, computed radial distribution functions (RDF)

confirmed large domain sizes with peak positions that match nicely to a perfectly ordered, hexagonal reference pattern (see Figure S2, Supporting Information). From the first peak of the RDF and its full-width-at-half-maximum (FWHM) we obtained an average center-to-center distance $d_{c-c} = 492 \pm 22$ nm. Figure 2b,c shows AFM images of the self-templated hc and Moiré structures. Both samples possess homogeneous monolayers with defined structural motifs on the area of the whole AFM image. Large single crystalline domains are observed with only few defects. Nevertheless, the degree of order is slightly reduced in comparison to the hexagonal array, which becomes visible by the number of higher order Bragg peaks in the FFT and the reduced positional correlation in the RDF of approximately 2–3 μm (Figure S2, Supporting Information). The sequential deposition of two hexagonal lattices that each are multidomain structures is responsible for the reduced domain size in the hc and Moiré samples. In the case of the hc lattice, the second monolayer deposits into the void of the first, deposited monolayer resulting in a smaller d_{c-c} (hc). The characteristic structure of the Moiré lattice is characterized by the angle of rotation α between the first and second deposited monolayer. The example shown in Figure 2c has a rotation angle $\alpha = 8^\circ$. The influence of the rotational angle on the Moiré lattices as well as additional AFM images including larger scan sizes for hc and Moiré lattices are shown in Figures S3–S5, Supporting Information. With our current self-assembly strategy, we do not have the precise control on domain orientation needed to prepare Moiré patterns with specific values of α at will. We see great potential to achieve a much better structural control by implementation of in situ diffraction analysis as a nondestructive tool to probe lattice geometries prior to transfer to any solid substrate. Our group is currently working toward this direction and results will be presented elsewhere.

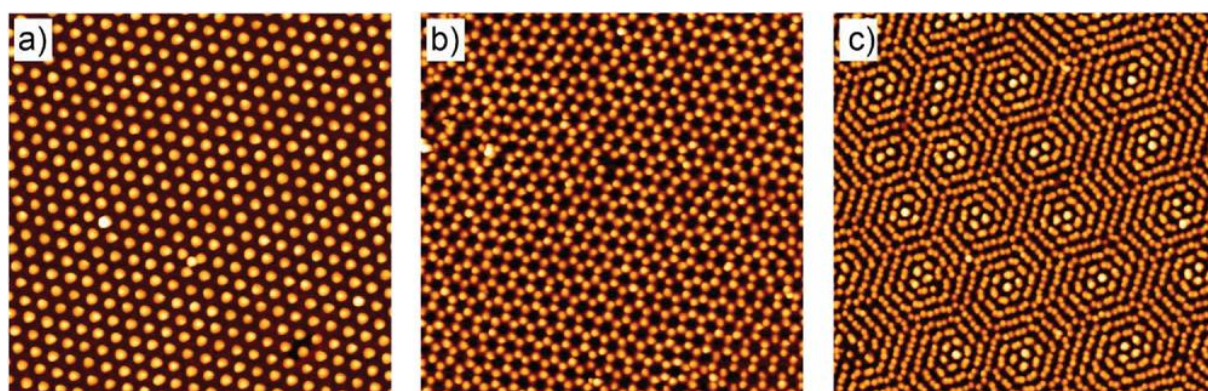


Figure 2. AFM height images of a) the first, hexagonally ordered monolayer, b) the hc structure after the second deposition and slow drying, and c) the Moiré structure after second deposition and fast drying.

In order to study the optical properties of the hc and Moiré structures, UV–vis absorbance spectroscopy was used and the results were compared to numerical FDTD calculations. We will start by addressing the optical properties of hc lattices.

Plasmon Resonance Coupling in Honeycomb Lattices

Figure 3 shows the development of the optical response of a monolayer sample during the various preparation steps used to produce an Ag-PNIPAM hc lattice. We directly compare experimental results from UV–vis absorbance measurements (a) to the respective theoretical spectra from FDTD calculations (b). Details on the simulation setup are provided in the Experimental Section and the Supporting Information. The dotted spectrum corresponds to the first, hexagonally ordered monolayer ($d_{c-c} = 492 \pm 22$ nm) shown in Figure 2a measured on a glass substrate against air in transmission geometry at normal incidence. The monolayer possesses a broad, dipolar LSPR with a maximum at 537 nm and a weak shoulder from a quadrupolar resonance contribution at 409 nm. The dipolar LSPR is red-shifted in comparison to the particles in dispersion ($\Delta\lambda = 37$ nm). This is caused by the increased effective RI environment with contributions from the supporting glass substrate ($RI_{\text{glass}} = 1.52$), the collapsed PNIPAM hydrogel shell ($RI_{\text{shell}} = 1.49$) and air ($RI_{\text{air}} = 1.00$).^{18, 57} On average this results in a higher effective RI of the environment compared to that of water with $RI_{\text{water}} = 1.332$. Due to the inhomogeneous RI environment coupling to the $\langle 0,1 \rangle$ Bragg mode is restricted.^{12, 18} The absorbance of the monolayer sample after deposition of a second Ag-PNIPAM monolayer with approximately the same d_{c-c} is shown in Figure 3a as long dashed line. Again, a broad, dipolar and a weak quadrupolar LSPR can be observed. The maximum intensity of the dipolar resonance has increased by approximately a factor of two, from 0.18 to 0.35, compared to the first hexagonal lattice. This increase matches perfectly to the increased number of particles after the second deposition. The average number of particles in a $10 \times 10 \mu\text{m}^2$ AFM scan has increased from 458 (first deposition) to 926 after the second deposition. This demonstrates that in both deposition steps nearly the same number of particles per area was applied. This also indirectly confirms that the first and the second hexagonal monolayer possess very similar values of d_{c-c} . The LSPR of the hc lattice is blue-shifted from 537 nm (first hexagonal lattice) to 507 nm indicating plasmon resonance coupling in the hc structure. This coupling occurs because of the reduced d_{c-c} (hc) of 295 ± 42 nm in the hc lattice. This distance is small enough to enable near-field plasmon resonance coupling.⁴⁸ However this resonance coupling is weak as evidenced by the large FWHM of the LSPR peak and the relatively small blue-shift as compared to the hexagonal monolayer. In order to enable far-field coupling to in-plane modes of diffraction, homogenization of the RI environment surrounding the particle

array is required.^{12-13, 19-20} We achieved this by spin-coating of a PNIPAM layer on top of the assembled structure.¹⁸⁻¹⁹ This lead to the absorbance depicted as solid line in Figure 3a. Additionally to the dipolar LSPR, which is reduced in intensity and width, a new feature, occurred at 638 nm. This surface lattice resonance (SLR) is a hybrid mode originating from coupling of the LSPR of the single particles to the $\langle 0,1 \rangle$ lattice mode. The reduction of the dipolar resonance width also leads to a seemingly more pronounced quadrupolar LSPR at approximately 427 nm. The fact that the LSPR is still strongly visible indicates a limited coupling strength to the Bragg mode in comparison to a perfect lattice in an effectively infinite RI environment, where the SLR is the dominating spectral feature.^{23, 37, 58} For our samples, the coupling strength is most probably restricted because of positional disorder and relatively small domain sizes.⁵⁹⁻⁶⁰ Field maps from FDTD calculations for hexagonally ordered arrays were previously reported by us and showed that the SLRs result from coupling of the dipolar LSPRs with the in-plane modes of diffraction.¹⁹ The quadrupolar mode occurs at too short wavelength to contribute to the diffractive coupling.

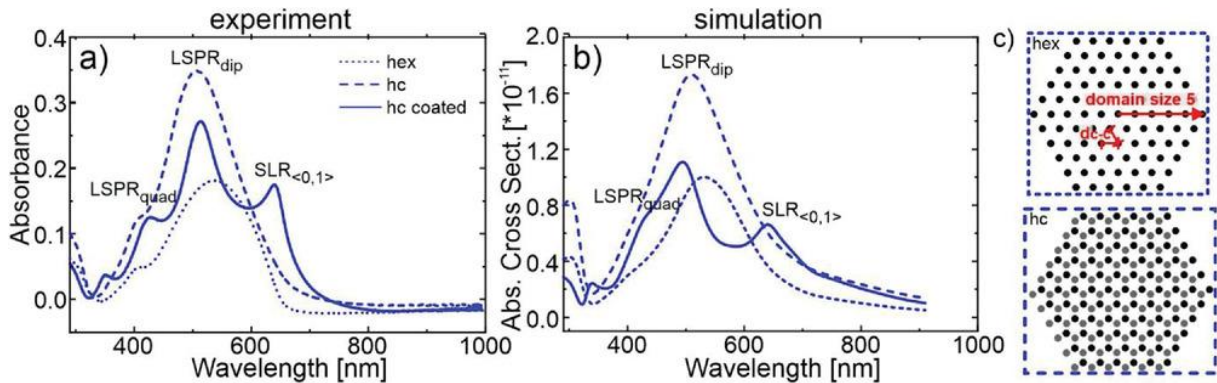


Figure 3. Optical characterization of different lattices. a) Experimental UV–vis absorbance spectra of hexagonally ordered Ag-PNIPAM particles on a glass substrate with $d_{c-c} = 492 \pm 22$ nm (dotted lines), after deposition of a second hexagonally ordered monolayer to create a self-templated hc structure (long dashed lines) and the hc structure coated with a film of PNIPAM with 240 nm thickness (solid lines). b) Complementary calculated absorbance spectra with finite domain size of five. The labels indicate the dipolar LSPR ($LSPR_{dip}$), the quadrupolar LSPR ($LSPR_{quad}$), and the SLR from coupling to the $\langle 0,1 \rangle$ Bragg mode. c) Sketches of finite lattices used in the simulation, where the hexagonal lattice consists of 91 particles (top) and the hc lattice of 182 particles (bottom).

Our experimental results for the hc lattices were confirmed with the calculated spectra depicted in Figure 3b. The hc lattice in the simulation is composed of two hexagonal sublattices with a domain size of five corresponding to 91 particles each (for comparison see the upper sketch in Figure 3c). The extinction cross-section was determined for a hexagonal silver particle monolayer with $d_{c-c} = 492$ nm (dotted line), an hc lattice (dashed line, sketch Figure 3c bottom, 182 particles), and the hc structure coated with 240 nm of PNIPAM (RI = 1.49, solid line).

Finite domain sizes were chosen in the simulations in order to account for the lattice imperfections of the experimental samples. The resonance positions determined with the finite lattice simulation (Figure 3b) match very well to the experimental results and give a LSPR at $\lambda_{\text{LSPR}} = 532$ nm for the hexagonal array, for the hc structure at $\lambda_{\text{LSPR}} = 510$ nm and an SLR for the coated sample at $\lambda_{\text{SLR}} = 639$ nm. The SLR of the experimental hc sample is less broad (FWHM = 64 nm, quality factor $Q = \text{FWHM}/\lambda_{\text{SLR}} = 10$) as compared to the SLR of the calculated finite array (FWHM = 129 nm, $Q = 5$). This indicates that our average experimental domain sizes are larger than five. Nevertheless, the relatively small domains and the multidomain character of our experimental samples lead to much weaker SLRs than in an infinite lattice, as the comparison to a simulation of an infinite periodic structure shows (Figure S6, Supporting Information).

In the following, we will address the influence of the lattice period and plasmonic nanoparticle composition on the optical properties of our hc lattices. Therefore, we prepared hc monolayers with a range of inter-particle spacings ($d_{\text{c-c}} = 432\text{--}512$ nm referring to the hexagonal sublattices, see Figure 3c). Lattices were prepared with the Ag-PNIPAM (Figure 4a; Figure S7a, Supporting Information) and the Au-PNIPAM microgels (Figure 4b; Figure S7b, Supporting Information). Furthermore, binary lattices using both types of core-shell particles were fabricated (Figure 4c; Figure S7c, Supporting Information). The latter binary lattices possess gold and silver nanoparticles at alternating positions. The spectra in Figure 4a–c show that all samples support SLRs. Furthermore, for each sample set, the SLRs red-shift with increasing $d_{\text{c-c}}$ as a consequence of the redshift of the diffractive modes. The theoretical $\langle 0,1 \rangle$ diffraction wavelengths shift from 554 nm for the sample with smallest $d_{\text{c-c}}$ to 656 nm for the largest spacing. In addition, the SLRs become less intense and the peak width increases as $d_{\text{c-c}}$ increases. At the same time, the lower wavelength spectral features associated with the single particle LSPR at approximately 500 nm become more pronounced. These effects are attributed to a decreasing coupling efficiency with increasing lattice period that can be attributed to the limited domain size in our multidomain samples and scattering losses that dampen the diffractive modes.¹⁷ The Ag-PNIPAM hc arrays show a quadrupolar LSPR contribution at approximately 410 nm (Figure 4a). As $d_{\text{c-c}}$ increases the intensity of the quadrupolar mode decreases, mainly caused by the decreasing number of particles per area. For the Au-PNIPAM hc arrays (Figure 4b) an LSPR at approximately 550 nm becomes more pronounced with increasing $d_{\text{c-c}}$, that again can be attributed to a decreasing coupling efficiency. In the spectra of the binary particle system (Figure 4c) the plasmonic contributions of both plasmonic materials, that is, the cores of the Au-PNIPAM and Ag-PNIPAM microgels, can be identified

in addition to the SLRs. This effect is best to be observed in the direct comparison of experimental spectra of hc samples with similar spacings consisting of Ag-PNIPAM ($d_{c-c} = 492 \pm 22$ nm, blue trace), Au-PNIPAM ($d_{c-c} = 492 \pm 26$ nm, red trace), and both particle types ($d_{c-c} = 490 \pm 36$ nm, green trace) shown in Figure 4d. The SLR positions (at approximately 635 nm) are hardly affected by the plasmonic core material. Only the position of the in-plane diffractive modes determines the SLR wavelength. At lower wavelength, in the spectral region of the uncoupled LSPRs, the spectra display either a resonance position characteristic for silver (blue trace) or gold (red trace) or of a mixed nature (green trace). Dipolar LSPRs at approximately 500 and 550 nm are present due to the Ag-PNIPAM and Au-PNIPAM particles, respectively, as well as the quadrupolar contribution from Ag-PNIPAM at approximately 410 nm.

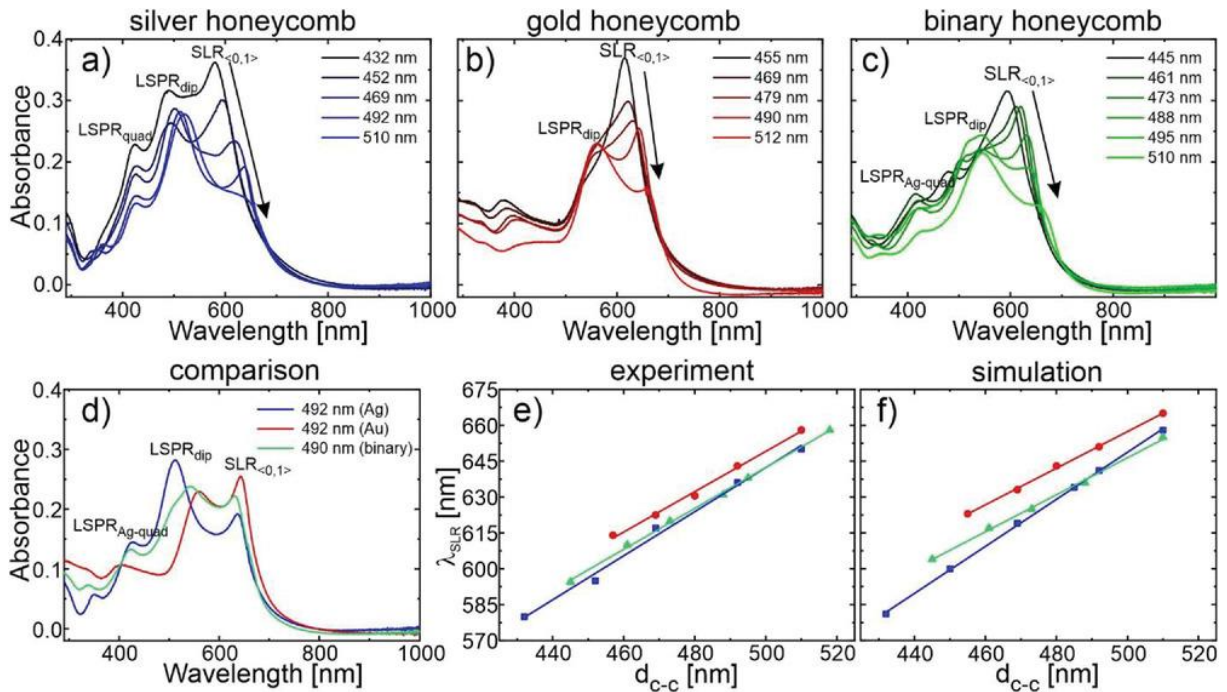


Figure 4. Influence of nearest neighbor center-to-center distance and nanoparticle material on the optical response. UV–vis absorbance spectra of a) Ag-PNIPAM, b) Au-PNIPAM, and c) binary nanoparticle hc lattices from experiment. Numbers in the legends refer to values of d_{c-c} corresponding to the initial hexagonal sublattices. d) Comparison of hc lattices with $d_{c-c} \approx 490$ nm consisting of Ag-PNIPAM particles (blue trace), Au-PNIPAM (red trace), and both particle types (green trace). e) Summary of the experimental SLR positions in dependence of d_{c-c} and material (Ag-PNIPAM: blue symbols; Au-PNIPAM: red symbols; binary lattice: green symbols). f) Respective results from FDTD calculations. The solid lines in (e) and (f) are linear fits to the data.

To study the local field enhancement and the coupling in the unary and binary hc lattices, we simulated near-field electromagnetic intensity maps (Figure S8, Supporting Information). Maps generated at the LSPR positions of the respective building blocks reveal the excitation of dipolar LSPR modes with indication for weak near-field coupling between nearest neighbor particles.

At the SLR positions, the field-maps show the typical diffraction mode structure related to coupling between the dipolar LSPRs and the in-plane $\langle 0,1 \rangle$ diffraction. The field strengths at the SLRs are higher than at the LSPRs in all samples. However, the field strength may not be directly translatable to our experimental arrays since the field-maps were calculated for infinite lattices due to computational reasons.

In Figure 4e (experiment) and 4f (simulation) the SLR wavelengths of all hc samples are plotted as a function of d_{c-c} . In these plots the same color code was used as for the spectra in Figure 4d. For all samples a linear dependence between the SLR position and d_{c-c} can be observed in experiment and simulation. In fact, the linear fits to the data (solid lines) describe all data in very good agreement confirming that all long-wavelength features are truly SLRs. The data for the different materials nicely overlap (similar slopes) and only the SLR values of the Au-PNIPAM hc lattices (red symbols) are slightly higher in comparison to the Ag-PNIPAM and binary hc lattices (blue and green symbols, respectively) at a given d_{c-c} . The calculated SLRs are shifted to slightly higher values (see Tables S1–S3, Supporting Information), which can be explained by the positional disorder in the experimental samples in comparison to the perfectly ordered arrays simulated. It was shown that disorder leads to a blue-shift of the SLR in comparison to a perfect lattice.⁵⁹

Plasmon Resonance Coupling in Moiré Lattices

Experimental spectra recorded from the Moiré monolayers (coated with a PNIPAM film of 240 nm thickness) prepared from Au-PNIPAM particles (red spectrum), Ag-PNIPAM particles (blue spectrum), and a binary lattice prepared from both particle types (green spectrum) are shown in Figure 5a. These samples have very similar d_{c-c} values ($d_{c-c} = 485\text{--}490$ nm) and thus are expected to show $\langle 0,1 \rangle$ diffraction modes at very similar wavelengths.³⁸ Independent of the plasmonic material, all samples support SLRs with a center wavelength of approximately 655 nm. At this point we want to emphasize that the SLR position in our experimental samples is an averaged response over many different Moiré motifs. Since we produce multidomain samples and every domain can possess a different angle α between the monolayer that was first deposited and the second one, we obtain many different Moiré patterns in one and the same sample (compare Figure S5b, Supporting Information). Measuring the absorbance of a mm²-sized area consequently produces an averaged optical response over many domains. Calculating the optical response of different Moiré patterns (Figure 5b: Ag-PNIPAM; Figure 5c: Au-PNIPAM) however shows that the SLRs in all cases lie in a similar wavelength range with only minor variations in dependence of α . In contrast, the optical response in the lower wavelength LSPR region is again determined by the plasmonic material that was used for the sample

preparation (see Figure 5a). In the case of the Ag-PNIPAM lattice the LSPR is located at approximately 500 nm (dipolar) and 425 nm (quadrupolar), for Au-PNIPAM at approximately 570 nm. The binary sample shows the quadrupolar resonance from the Ag-PNIPAM particles and a broad resonance at 543 nm originating from the underlying dipolar resonances of both plasmonic cores.

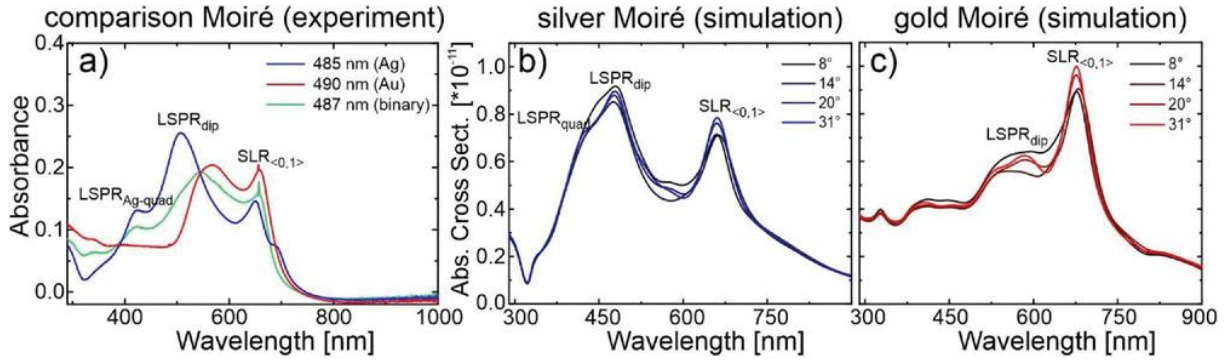


Figure 5. SLRs in Moiré structures: a) Experimental UV–vis absorbance spectra of Ag-PNIPAM (blue trace), Au-PNIPAM (red trace), and binary (green trace) Moiré lattices. Calculated spectra with different degrees of rotation between first and second deposited monolayer of the Moiré structure for b) Ag-PNIPAM (black to blue) and c) Au-PNIPAM (black to red).

Influence of Lattice Symmetry on Resonance Coupling

At last, we want to investigate the influence of the lattice symmetry on the SLRs. Therefore, we compare Ag-PNIPAM lattices with hexagonal (dotted line), hc (solid line), and Moiré (dotted-dashed line) lattice geometries in Figure 6a. The samples have very similar periodicities, that is, the starting monolayers with hexagonal order have approximately the same inter-particle spacing ($d_{c-c} = 483\text{--}488\text{ nm}$). The SLRs of the hexagonal and Moiré structures almost perfectly overlap with resonance positions of $\lambda_{\text{SLR}} = 651\text{ nm}$ and $\lambda_{\text{SLR}} = 650\text{ nm}$, respectively. Only the SLR of the hc structure is significantly blue-shifted to $\lambda_{\text{SLR}} = 629\text{ nm}$. This blue-shift of the hc structure in comparison to hexagonal lattice symmetries was also demonstrated in lithographically prepared samples by Humphrey and Barnes³⁷ and confirmed by calculations using a modified long-wavelength approximation (MLWA). They found that the intersection of the real part of the array factor S with the inverse of the polarizability α determines the exact SLR position. In other words, the lattice periodicity and structure as well the wavelength dependent polarizability are the key parameters that define the SLR. The absorbance intensity of the hc and Moiré spectra in the LSPR region is roughly doubled in comparison to the hexagonal array. This is related to the increased number of particles per area due to the double deposition process. The same trend can be found in the comparison of gold arrays with different lattice symmetries (Figure 6b, $d_{c-c} = 481\text{--}484\text{ nm}$). The hexagonal sample

exhibits an SLR of $\lambda_{\text{SLR}} = 654$ nm, the Moiré structure of $\lambda_{\text{SLR}} = 651$ nm and the hc structure a clearly blue-shifted SLR of $\lambda_{\text{SLR}} = 633$ nm. Lastly the binary array structure which only exists as a Moiré and hc lattice (Figure 6c, $d_{\text{c-c}} = 487$ –488 nm) gives very similar results with SLRs at $\lambda_{\text{SLR}} = 643$ nm and $\lambda_{\text{SLR}} = 631$ nm, respectively. Our experimental results were also confirmed with simulations for the silver and the gold arrays and are depicted in Figure S9, Supporting Information.

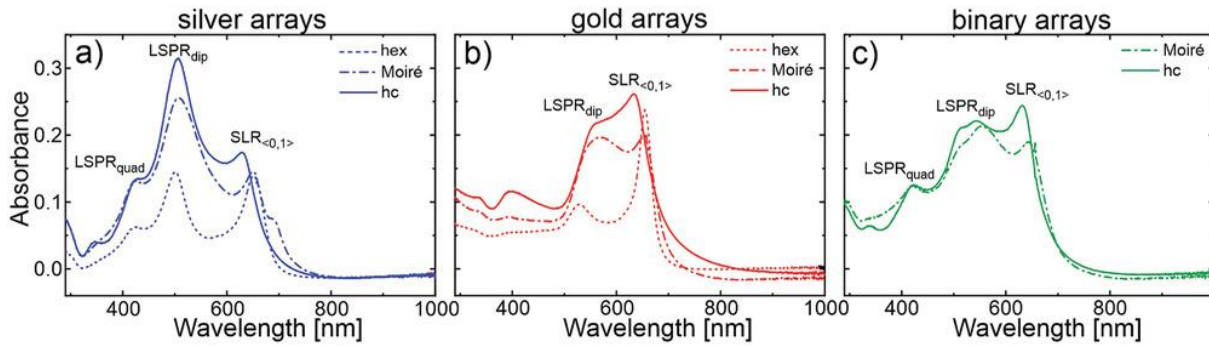


Figure 6. Influence of lattice geometry. Experimental UV–vis absorbance spectra of a) silver (blue traces, $d_{\text{c-c}} = 485$ nm), b) gold (red traces, $d_{\text{c-c}} = 483$ nm), and c) both types of nanoparticles (green traces, $d_{\text{c-c}} = 488$ nm) in a hexagonal array (dotted line), honeycomb structure (solid line), and Moiré structure (dotted-dashed line).

In this direct comparison of different lattice geometries one can also see that the hexagonal lattice supports the most pronounced SLRs. This becomes particularly obvious when comparing the relative peak intensities of the SLRs and the plasmonic contributions at lower wavelengths. The fact that the hexagonal lattices show the strongest plasmonic/diffractive coupling can be explained by the larger single crystalline domains and lower defect density as compared to the other two structures. The double deposition used for the preparation of the hc and Moiré lattices increases the number of defects and domain boundaries which are inherent to the monolayer. This leads to reduced domain sizes in the hc and Moiré lattices and therefore weaker SLRs. The fact that SLRs are nevertheless visible in our cm^2 -sized, multidomain samples proves the robustness of SLRs with respect to structural imperfections. As our self-assembly process is fast, reproducible and cost- and energy-efficient, we believe that it can be of interest for nanooptical applications that employ such optically functional lattices, for example, in lasing and sensing applications. For this, ultimately optical losses need to be reduced and consequently the quality factor of the SLR needs to be improved. This most likely cannot be done by optimization of a single parameter. We believe that increasing the domain sizes and using larger plasmonic nanoparticles with higher scattering cross-sections and shifting the diffractive modes further toward the infrared could lead to significantly enhanced SLRs. Nevertheless, we want to point out that on a 1 cm^2 area of the samples presented in this study, the self-templated

assemblies contain approximately 10×10^{10} particles. Assembly on larger substrates is easily possible as the size limiting factor is predominantly the container used for the interface assembly—in our case a crystallizing dish with 6 cm diameter requiring approximately 0.07 mg of core-shell particles to fully cover the air/water interface with a periodic monolayer. We kindly guide the reader to the video of the assembly protocol recently published as Supporting Information in another publication by us.¹⁷

Conclusion

In conclusion, we have produced periodic plasmonic particle lattices with hexagonal, honeycomb, and Moiré structures through self-assembly of wet-chemically synthesized colloidal building blocks on macroscopic substrates. All lattices support SLRs as a consequence of plasmonic/diffractive coupling. The lattice type has only minor impact on the SLR position in agreement to previous results from Humphrey³⁷ and Guo³⁸ for lithographically prepared samples. However, the strength and position of the SLRs depend on the lattice constant and the degree of order. By using core-shell microgels with either gold or silver cores, lattices with different LSPR properties were produced. The observed SLR positions are fairly independent of the plasmonic material even in binary lattices that feature both types of plasmonic nanoparticles in one superstructure. The binary systems support SLRs and also feature plasmonic contributions related to both materials. At the same time we did not observe evidence for synergistic optical effects in these heterogeneous samples.

This work offers a direct comparison of the optical properties from hexagonal, honeycomb and Moiré type samples and shows that the SLR is a very robust feature. In fact, small domain sizes with less than 100 particles are sufficient to support SLRs. The most pronounced SLR was obtained for a hexagonal lattice, which possesses the largest single crystalline domains and lowest defect density. While the coupling strength of the presented lattices is limited due to structural imperfections and limited domain sizes, we envision heterogeneous Moiré lattices to be particularly interesting for studying electromagnetic near- and far-field as well as emitter-metal absorber coupling as recently demonstrated by Aftenieva.⁶¹

Experimental Section

Materials

Gold(III)chloride trihydrate (Sigma-Aldrich, $\geq 99.9\%$), sodium citrate dihydrate (Sigma-Aldrich, $\geq 99\%$), butenylamine hydrochloride (Sigma-Aldrich, 97%), sodium dodecyl sulfate (Merck), *N*-Isopropylacrylamide (NIPAM; Sigma-Aldrich, 97%), *N,N'*-methylenebisacrylamide (BIS; Sigma-Aldrich, 99%), potassium peroxodisulfate (Fluka, $\geq 99\%$), silver nitrate (99.999%, Sigma), ascorbic acid (p.a., Roth), acetonitrile (HPLC grade,

Fisher Chemicals), cetyltrimethylammonium chloride (CTAC, Sigma-Aldrich, 25 wt% in water), ethanol (p.a., Honeywell), and Hellmanex III (Hellma GmbH) were used as received. Water (MQ water) was purified by a Milli-Q system (Millipore) leading to a final resistivity of 18.2 MΩ cm. MQ water was used for all synthesis, purification, and assembly steps. Substrates for the self-assembly procedures were prepared by cutting pieces of approximately $1 \times 1 \text{ cm}^2$ from standard microscope glass slides of 1 mm thickness (Menzel-Gläser, Thermo Scientific).

Particle Synthesis

Core-shell microgels with nearly spherical gold nanoparticle cores of approximately 14 nm in diameter and chemically cross-linked polymer shells composed of poly(*N*-isopropylacrylamide) (PNIPAM) were prepared by seeded precipitation polymerization.⁵⁵ These core-shell particles possessed a total hydrodynamic diameter of 336 nm (20 °C, swollen state) as measured by dynamic light scattering. In the following the gold cores were overgrown with either gold (Au) or silver (Ag) to produce core-shell microgels with plasmonic cores of approximately 100 nm diameter. The overgrowth procedure with gold was adopted from Honold *et al.*⁴⁸ Overgrowth using silver was performed as previously published by Volk *et al.*¹⁸ Further details on all synthesis steps can be found in the Supporting Information. In the following the two microgel systems would be referred to as Au-PNIPAM and Ag-PNIPAM.

Preparation of Hexagonal, Honeycomb, and Moiré Lattices

Hexagonally ordered monolayers of the core-shell microgels were prepared at air/water interfaces and then transferred onto glass supports following a recently published protocol.⁴⁸ Subsequently, the obtained monolayer samples with hexagonal order were used for a second monolayer deposition step. Slow drying of the second monolayer on top of the first one resulted in honeycomb lattices while fast drying led to Moiré lattices. A detailed description of the assembly process is given in the Supporting Information. Results from Brownian dynamics simulations on the structural formation process nicely matching the experimental findings were recently published by Volk *et al.*⁵³ In order to enable the formation of SLRs the self-assembled arrays were overcoated with linear PNIPAM ($40\,000 \text{ g mol}^{-1}$) synthesized following a protocol from Ebeling *et al.*⁶² For the coating 40 μL of a PNIPAM solution (40 mg in 1 mL 1,4-dioxane) was evenly distributed onto the substrate and then deposited via spin-coating at 2000 rpm for 90 s resulting in a layer thickness of 240 nm.

Transmission Electron Microscopy

The Ag-PNIPAM and Au-PNIPAM core-shell microgels were characterized by TEM using a ZEISS CEM 902 operated in bright field mode. The acceleration voltage was set to 80 kV. All samples were prepared by collecting a floating particle monolayer from the air/water interface

onto carbon coated TEM grids (copper, 200 mesh). TEM images were analyzed using the ImageJ software. The sizes of the metal cores were determined by measuring at least 150 particles from several TEM images.

Atomic Force Microscopy

$10 \times 10 \mu\text{m}^2$ and $40 \times 40 \mu\text{m}^2$ topographic AFM images were recorded with a Nanowizard 4 (JPK Instruments) using OTESPA-R3 AFM probes (Bruker). The cantilevers possess a resonance frequency of approximately 300 kHz and a spring constant of approximately 26 N m^{-1} . The tip geometry was a visible apex with a nominal tip radius of 7 nm. Dry samples were imaged in intermittent contact mode against air. Inter-particle distances were obtained by computing the radial distribution functions (RDF) using the x, y positions of the particle centers.

Extinction Measurements

Extinction measurements were conducted on a Specord S600 UV–vis spectrometer (Analytik Jena AG). Spectra from dilute particle dispersions were recorded in a wavelength range of 250–1019 nm in transmission geometry using quartz cuvettes with 1 cm path length (Hellma Analytics). The particle assemblies on glass substrates were positioned vertically in the light path using a solid sample holder. All spectra were background and substrate corrected, using a reference sample, either a cuvette filled with water or a clean glass substrate. The obtained data were converted into absorbance spectra.

Finite Difference Time Domain Simulations

The optical responses in transmission and reflection (infinite array, adapted from ref. ¹⁸) or absorption and scattering (finite array) were simulated using a commercial software from Lumerical Solutions, Inc. (FDTD Solutions, Version 8.18.1332). A hexagonal or honeycomb nanoparticle array was used (compare Figure S4d, Supporting Information) and periodic boundary conditions (BC) were applied in x, y -direction (layer direction) and perfectly matched layer (PML) BC in z -direction (beam direction) in order to simulate infinite arrays. As light source a linear polarized plane wave source oriented along the z -axis was employed. Values for particle diameters, periodicities, multilayer materials, and thicknesses were taken from the experimental findings. The FDTD simulation total length in z -direction was chosen to be $3.5 \mu\text{m}$ and transmission monitors were located at both ends. Then the simulation setup was placed in the center of this simulation box and the plane wave light source was injected from within the glass substrate. A polynomial function is employed by the FDTD software to approximate the refractive index (RI) of silver⁶³ and gold⁶⁴ to literature values in order to perform a broadband source simulation ($\lambda = 290\text{--}910 \text{ nm}$) while taking the wavelength dependence of the metals into account. For the other materials only a minor change in the RI

was expected over the studied wavelength range. Therefore, the glass substrate was simulated with a constant RI of 1.52, the air background with an RI of 1, and the dry PNIPAM shell around the plasmonic particles and the coating with 1.49. The latter value was slightly smaller than reported by Brasse *et al.*⁶⁵ (1.50) to take some residual water in the collapsed PNIPAM shells into account. An isotropic mesh overwrite region was used according to the specific periodicity and particle diameter (mesh always 3.5 nm). All simulations reached the auto shut-off level of 10^{-6} before reaching 1000 fs simulation time.

A hexagonal, Moiré, or honeycomb nanoparticle array (domain size of 5 referring to the number of particle rings around the center particle, compare Figure S4c, Supporting Information) with perfectly matched layer (PML) boundary conditions in x -, y -, and z -direction was used in order to simulate finite arrays. A total-field scattered-field source (TFSF) surrounding the nanoparticle array was used as light source (incident wavelengths: $\lambda_{\text{inc}} = 290\text{--}910$ nm). There were two analysis groups employed, each of which consisted of a box of power monitors: one in the total field region and one in the scattered field region. These analysis groups were used to calculate absorption and scattering. The same RI settings as for the infinite array were used. An overwrite region with a uniform mesh of 5 nm in the monolayer area was chosen additionally to the nonuniform mesh. All simulations reached the auto shut-off level of 10^{-6} before reaching 1000 fs simulation time.

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Supporting Information

Particle Synthesis

The core-shell particles were synthesized in three steps following a recently published protocol.¹ First gold nanoparticles were synthesized according to the well-established Turkevich method.² Briefly, 200 mL of an aqueous HAuCl_4 solution ($5 \cdot 10^{-4}$ M) were brought to heavy boiling under continuous stirring. Then 10 mL of a hot aqueous solution of sodium citrate dihydrate (1 wt.-%) were added quickly to the boiling solution. After 20 min reaction time, the now deeply red dispersion was cooled to room temperature under continued stirring. Next, the obtained gold nanoparticles were encapsulated in chemically cross-linked poly(*N*-isopropylacrylamide) (PNIPAM) shells by seeded precipitation polymerization.³ For this, 1.2 mL of an aqueous SDS solution (0.624 mM) were added to the freshly prepared gold particle dispersion and stirred for 20 min in order to stabilize the particles. Then 0.392 mL of an aqueous butenylamine hydrochloride solution (2.88 mM) were added dropwise under further stirring. After 20 min the gold nanoparticles were concentrated and purified from excess citrate using four centrifugation steps, each for 90 min at 3300 rcf. Redispersion following the last centrifugation step was done with as little MQ water as possible in order to obtain a concentrated dispersion. Next a total of 100 mL of water containing 0.06 M NIPAM and 15 mol% of BIS (referred to the amount of NIPAM) were heated to 70 °C and degassed with nitrogen for 30 min in a three-neck round-bottom flask equipped with a reflux condenser. Afterwards, 2.35 mL of the dispersion of functionalized gold nanoparticles ($[\text{Au}] = 0.01$ M) were added dropwise. After 15 min of equilibration, the polymerization was started by the rapid addition of 2 mg potassium peroxodisulfate dissolved in 1 mL of water. The polymerization was allowed to proceed for two hours and then slowly cooled to room temperature. Cleaning of the core-shell particles was done via repeated centrifugation (3 times, 90 min at 6500 rcf) and redispersion of the residue in water. Finally, the particles were concentrated to yield an aqueous dispersion of 2 wt.-%. After these two steps core-shell particles with spherical cores of approximately 14 nm in diameter and hydrogel shells with an overall hydrodynamic diameter of 336 nm (20 °C, swollen state) were obtained.

In a third step the cores of these core-shell particles were either overgrown with gold (Au) or silver (Ag) aiming at core sizes of approximately 100 nm in diameter for both plasmonic materials. Overgrowth with gold was performed following the procedure reported by Honold *et al.*⁴ For this 100 μL of the 2 wt.-% stock dispersion of the core-shell particles (small Au cores) were diluted with 100 μL of an aqueous CTAC solution (100 mM) in order to obtain the precursor solution. Next the feed solution containing 0.5 mM HAuCl_4 and 4.75 mM CTAC was prepared. Now the precursor solution was added to 8 mL of a 2.4 mM CTAC solution under

heavy stirring in an Erlenmeyer flask, followed by the addition of 83 μL of freshly prepared ascorbic acid solution (10 mM). Next, 1.280 mL feed solution was added dropwise under stirring and the reaction was allowed to proceed for 30 min. The addition of ascorbic acid and feed solution was repeated for another four times until the desired core size was achieved. The growth process was monitored by UV-vis spectroscopy. After each growth step, a small volume of the reaction mixture was extracted and diluted with water in order to determine the LSPR position of the core-shell particles, which correlates with the particle size. Purification of the particles was done using centrifugation at 3740 rcf for 30 min. The supernatant was discarded and the precipitate was redispersed in water for three times and as a last step concentrated in ethanol.

For the overgrowth of the initial core-shell particles with silver, the protocol by Volk *et al.* was used.¹ 79 μL of the stock dispersion of the core-shell particles (small Au cores) were mixed with 2.65 mL of MQ water and 0.5 mL acetonitrile in a round bottom flask placed in an ice-bath. Then, 2 mL of an ice-cold ascorbic acid solution (49 mM) and 5.05 mL of a silver nitrate solution (15 mM) were added under stirring one after the other. After 30 min of reaction time the dispersion was allowed to warm up to room temperature by removal of the ice bath. Purification was performed as described above, but instead of MQ water ethanol was used twice for redispersion of the precipitate. The final concentration was adjusted to approximately 1 wt.-%.

For simplicity we use the notations Au-PNIPAM and Ag-PNIPAM for the two core-shell systems with overgrown cores referring to the approximately 100 nm diameter silver (Ag) and gold (Au) cores. In this nomenclature and in our discussion we omit that the silver cores of the Ag-PNIPAM particles carry small gold particles that were used as the initial seeds for the overgrowth. Since > 99% of the metal core volume is silver, the presence of the central gold nanoparticle is not contributing to the extinction of the overall particles.

Interface-assisted assembly and double deposition

The hexagonally ordered, honeycomb and Moiré arrays were prepared following a procedure published recently.⁵ Therefore, glass substrates were cleaned by sonication in aqueous Helmanex solution (2 vol.-%) for 15 min. Then the substrates were rinsed with water and further sonicated for 15 min in water. Finally rinsing and sonication in ethanol was applied for 15 min, followed by drying with compressed, dry nitrogen. Then the core-shell particles in ethanolic dispersion were slowly and steadily dispensed to the air/water interface. Immediately the particles formed a hexagonally ordered monolayer, which was subsequently transferred onto

the freshly cleaned glass substrates (1 cm^2 in size) by careful immersion of the substrate below the monolayer and retraction at an angle of 45° . The particle monolayer attached spontaneously to the glass surface. It was dried by blowing with a heat gun to the back of the substrate in order to adhere the particles more firmly to the substrate. By adjusting the dwell time of the freely floating monolayer at the air/water interface the center-to-center distance between the particles was tuned.⁶ Honeycomb and Moiré lattices were then prepared by a second monolayer deposition onto a substrate that already carried a single hexagonally ordered particle monolayer. Therefore, the coated substrate was pre-treated by oxygen plasma for 15 s and then immersed into a crystallizing dish filled with MQ-water at a 90° angle. Then a fresh monolayer was prepared at the interface as described above. Now the substrate was slowly retracted through the floating monolayer while maintaining the 90° angle. For Moiré lattices the sample was dried rapidly using the heatgun as for the first monolayer. In contrast, the substrate was left to dry slowly at room temperature, keeping the 90° angle, in order to obtain honeycomb lattices. Further details on the structure formation and the processes during the sequential double deposition of hexagonally ordered monolayers can be found in our recently published work.⁵

Histograms of particle core diameters

The average diameter and its standard deviation of the gold and silver cores were determined by TEM. Thanks to the large contrast difference between the metal cores and the PNIPAM shells, the core size can be directly determined precisely from TEM images of the Au-PNIPAM and Ag-PNIPAM core-shell particles. Figure S1 shows the corresponding size analysis and representative TEM images.

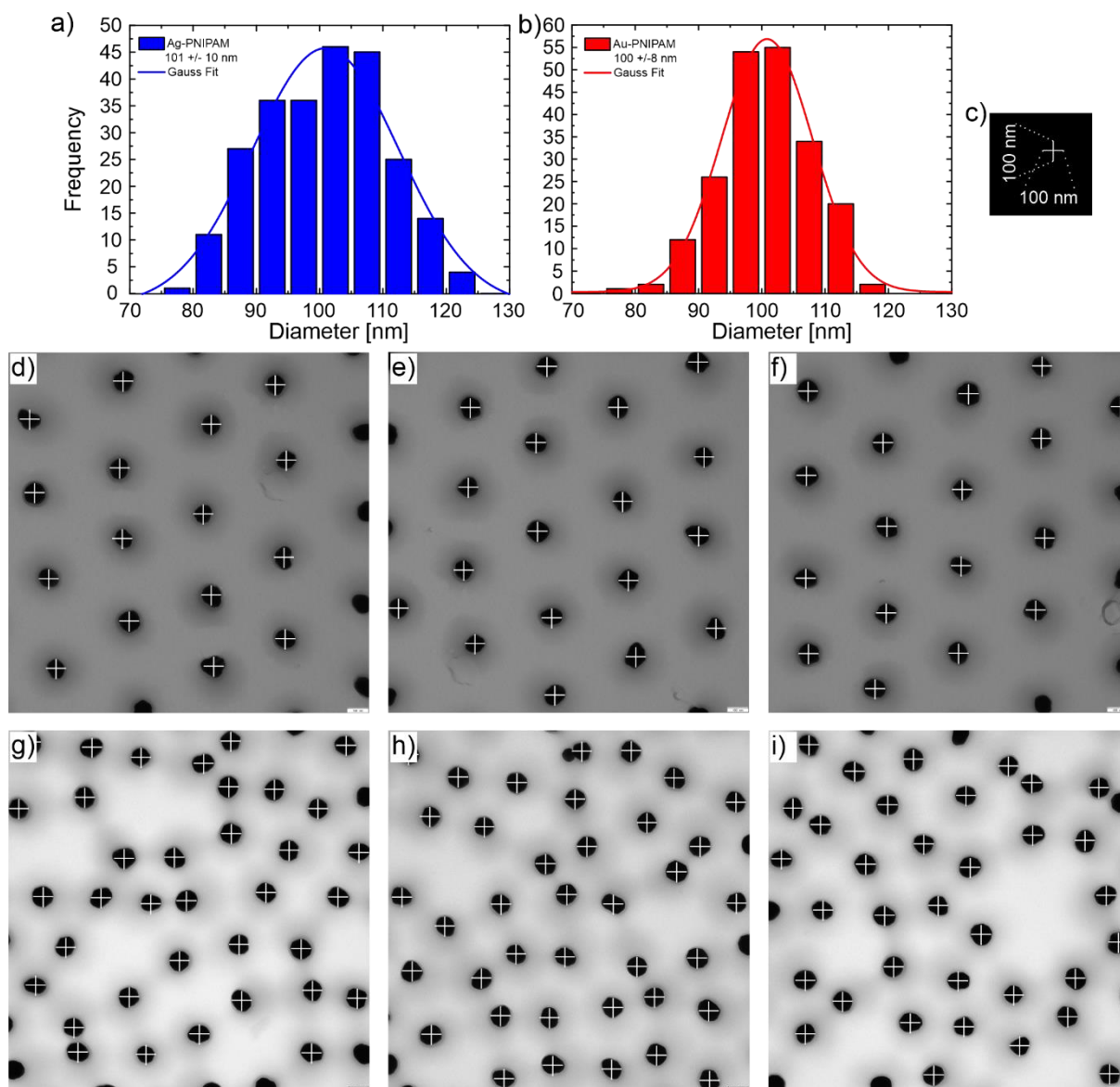


Figure S1. Histograms of particle size distributions obtained from TEM images of (a) Ag-PNIPAM cores and (b) Au-PNIPAM cores. (c) White cross used as scale bar in (d) to (i) with 100 nm in x and 100 nm in y direction. Examples of TEM images of Ag-PNIPAM in (d)- (f) and of Au-PNIPAM in (g)- (i).

Detailed description of sample preparation

In order to prepare well-ordered colloidal monolayers with either hexagonal (hex), honeycomb (hc) or Moiré structures, we used self-assembly of the core-shell microgels at the air/water interface.⁵ This method allows for the preparation of macroscopically sized, periodic particle arrays with tunable inter-particle distances.⁶ Briefly, a freely floating monolayer of the desired core-shell colloids was prepared at the air/water interface as the general first step. This monolayer was then collected onto a 1x1 cm², hydrophilic glass substrate at an angle of approximately 45°. The sample size is very flexible and only limited by the crystallizing dish, which dictates the monolayer area. Immediately after the transfer, the freshly coated substrate was dried by carefully blowing with a heatgun against the back of the substrate. This method

was found to assist maintaining the high degree order of the monolayer during drying^{4, 6} and also attaches the particles more firmly to the substrate. The latter effect is a prerequisite for the second assembly step where detachment of the particles from the first layer upon immersion into water needs to be avoided. Figure S2a schematically depicts the resulting monolayer after the first deposition. Here, for simplicity only the cores (blue circles) are depicted. The center-to-center nearest neighbor distances, d_{c-c} , are indicated as black lines connecting neighboring particles. The experimental result from the first monolayer deposition is shown in Figure S2d. The AFM height image reveals the regular hexagonal arrangement of the core-shell particles. The pronounced Bragg peaks from the Fast Fourier Transformation (FFT) in g) show a six-fold symmetry confirming the hexagonal order of the array. Long range order is demonstrated by the multiple orders of Bragg peaks. The radial distribution function (RDF, inset Figure S2g), also proves the hexagonal lattice symmetry. The red ticks indicate the theoretical peak positions of a perfect, hexagonally ordered reference pattern. The theoretical positions match very well to the experimental peaks.⁶⁻⁸ The first peak of the RDF was used to determine d_{c-c} . The full-width at half maximum (FWHM) of the peak was taken as a measure for the standard deviation of d_{c-c} ($d_{c-c}(\text{hex}) = 492 \pm 22$ nm).

For the preparation of hc and Moiré lattices, the coated substrates were employed for a second monolayer deposition using an approach that we have published very recently.⁵ Briefly, the substrate carrying the first monolayer was completely immersed into the aqueous phase at a 90° angle (vertically). Then a fresh, freely floating particle monolayer was prepared at the air/water interface in the exact same manner as the first monolayer was prepared at the interface. Now the immersed substrate was slowly retracted from the water subphase through the floating monolayer while maintaining the 90° angle. Depending on the drying conditions hc and Moiré lattices can be realized reproducibly: Slow drying of the second monolayer on top of the first one was used to prepare hc lattices, while fast drying resulted in Moiré lattices. Since the substrate needs to be immersed completely into the subphase the depth of the crystallizing dish is the limiting factor for the accessible sample area of the final honeycomb/Moiré structure. Figure S2b and c schematically depict the structure of the samples after the second monolayer deposition. Here, the blue circles represent the cores from the first deposited monolayer and the red circles correspond to the cores from the second deposition. The values of d_{c-c} , related to the hexagonal (sub-)lattice are indicated in (a) and (b). In (b) also the nearest neighbor distance between a particle from the first and a particle from the second deposition, $d_{c-c}(\text{hc})$, is indicated. The rotational angle α in the Moiré monolayer corresponds to the angle between the first and

second hexagonal lattice. Figure S2e and f show AFM images of the experimentally prepared hc and Moiré structures.

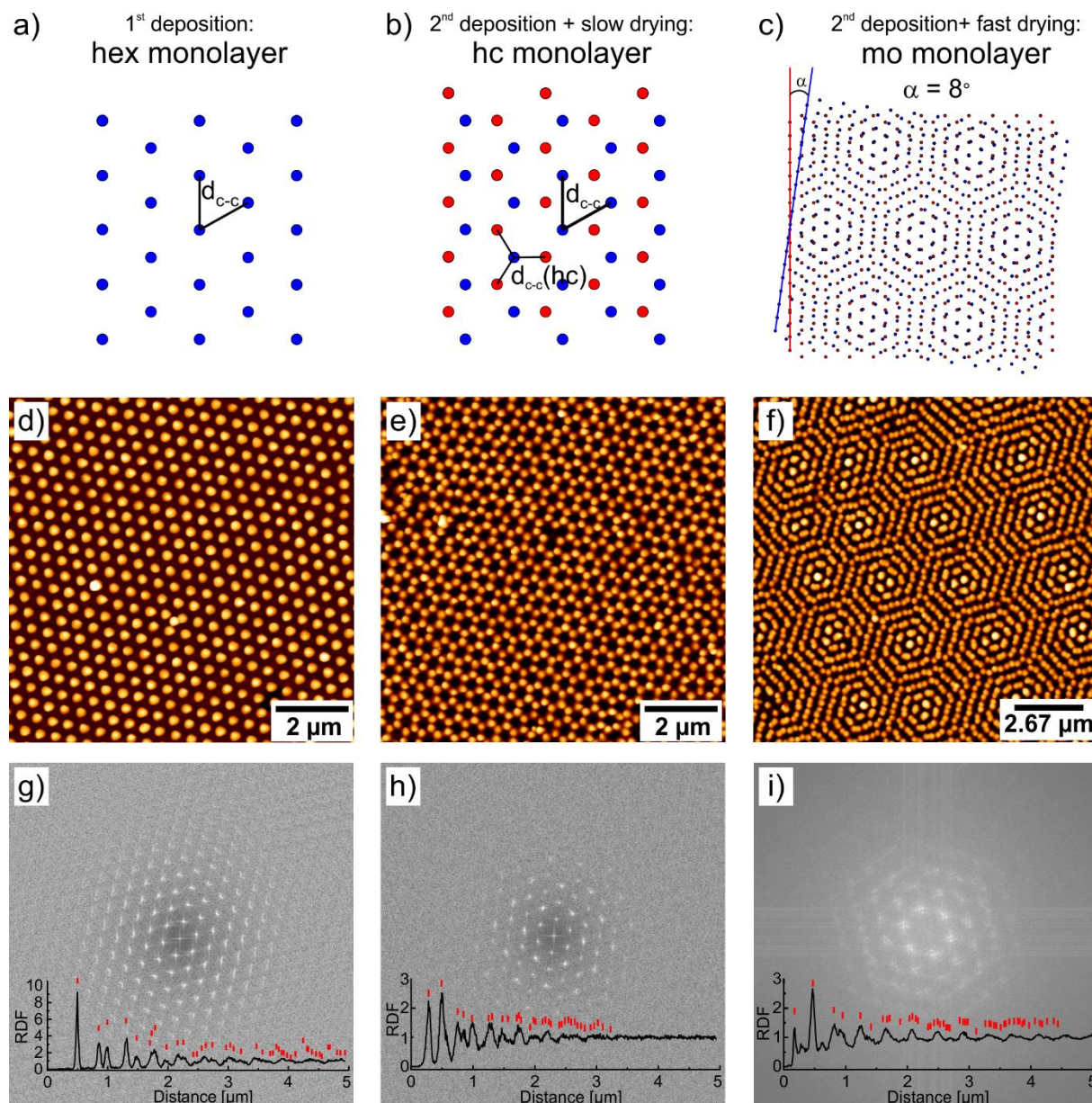


Figure S2. Characterization of different monolayer structures: Schematic depiction of (a) hexagonally ordered particle monolayer (cores only, blue circles) formed after the first deposition with center-to-center nearest neighbor distance d_{c-c} . (b) hc monolayer after second deposition (cores only, red circles) and applying slow drying conditions. Hexagonal sublattices with d_{c-c} from the hc lattice with new center-to-center nearest neighbor distance $d_{c-c}(hc)$ (c) Moiré monolayer after second deposition and applying fast drying conditions. The rotational angle α between the first and second deposition determines the specific motif. AFM height images of (d) first, hexagonally ordered monolayer, (e) hc structure after second deposition and slow drying, and (f) Moiré structure after second deposition and fast drying. FFTs with RDFs as insets for (g) hexagonally ordered monolayer, (h) hc structure and (i) Moiré lattice. The red ticks in the RDF plots show the theoretical peak positions in the RDF calculated for the respective perfect lattices.

Both samples possess homogeneous monolayers with defined structural motifs over the whole AFM image. Large single crystalline domains are observed with only few defects. The bright particle spots in the center of the Moiré motif in Figure 2f indicate an increased height of the array at this position. It is caused by the overlap of two particles at the center and also a partial particle overlap in the second level of the motif can be witnessed (compare Figure S2c) as the particles cannot sit in the same position as the particles of the first deposited monolayer.⁵

Since the hc structure is composed of two hexagonally ordered sublattices, that possess only a translational offset, also the corresponding FFT in Figure S2h shows a six-fold symmetry. Compared to the hexagonal monolayer, the degree of order is slightly reduced as visible by the reduced number of higher order Bragg peaks in the FFT. This is also confirmed by the RDF (inset Figure S2h) that shows clear positional correlations only up to about 2-3 μm . The reduced domain size results from the double deposition of individual hexagonal monolayers that each are multidomain structures. This effect will be discussed more closely in the next chapter. The first correlation peak in the RDF of the hc structure appears at significantly smaller distances as compared to the hexagonal monolayer and corresponds to the smaller $d_{c-c}(\text{hc})$. For a perfect hc lattice, the ratio $d_{c-c}(\text{hex})/d_{c-c}(\text{hc})$ is expected to be $\sqrt{3}$, associated with the deposition of each particle from the second monolayer into the voids formed by three particles of the first monolayer. The red ticks from an ideal hc reference lattice in the RDF plot are again in good agreement with the peak positions from experiment.

As explained above, the exact motif of the Moiré structure depends on the rotational angle α between the first and the second hex monolayer. The Moiré structure depicted in Figure S2f results from an angle of rotation $\alpha = 8^\circ$ (compare theoretical structure in Figure S2c). The FFT (Figure S2i) also possesses a six-fold symmetry, but the reflexes are broader as compared to the hexagonal and hc lattices. Again, the red ticks from an ideal Moiré reference lattice in the RDF plot (Figure S2i) are in good agreement with the peak positions from experiment. Additional AFM images including larger scan sizes for a hc and a Moiré lattice are shown in Figure S5.

Moiré lattices formed for different rotation angles α

Figure S3 demonstrates how the rotation angle α between the hexagonally ordered monolayers of the first (red circles) and second (blue circles) deposition influences the final 2D Moiré array. From a) to d) α is increased from 8° to 31° .

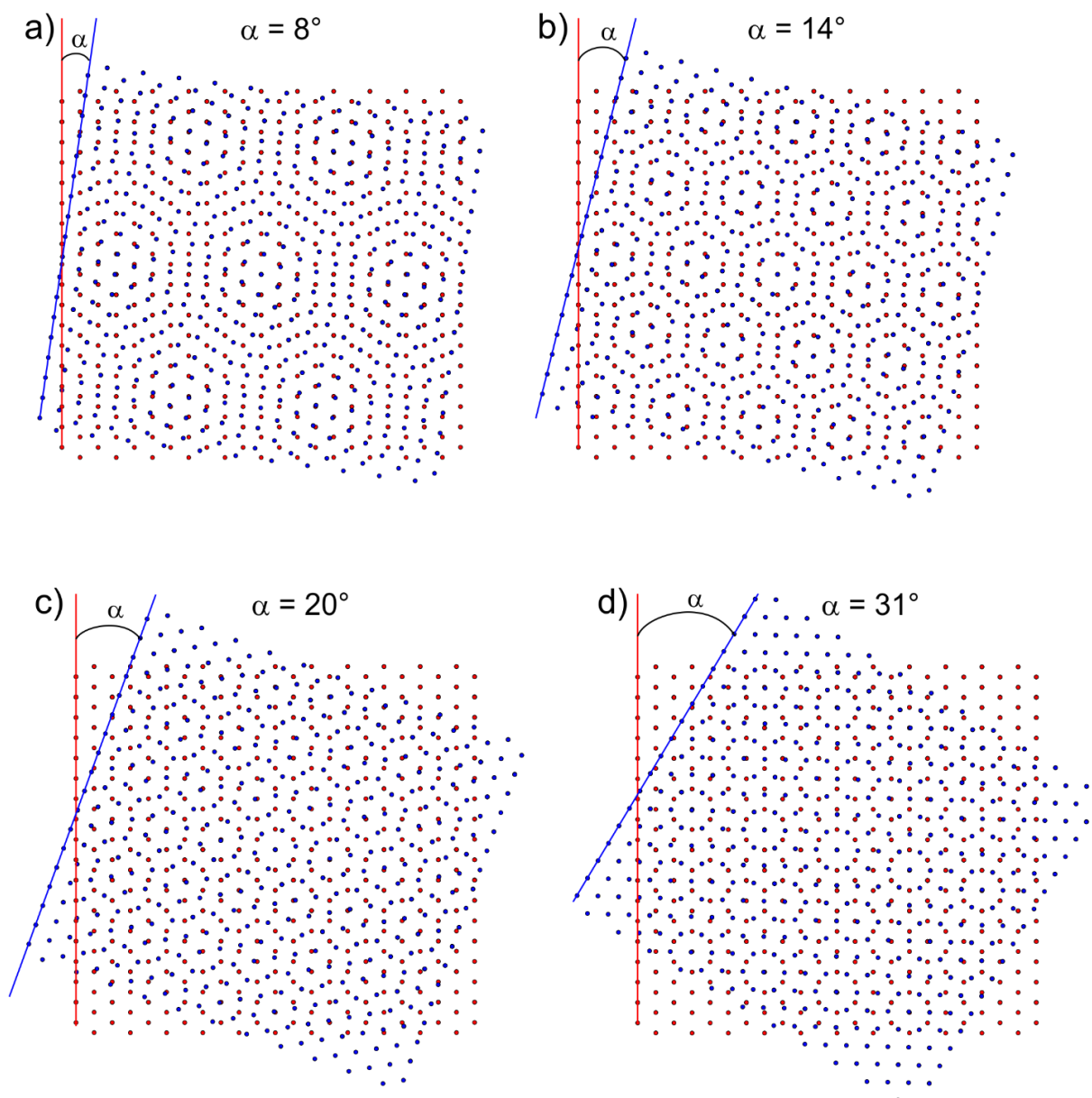


Figure S3. Moiré arrays for different rotation angles α .

Figure S4 shows experimentally observed Moiré arrays from different locations on a single substrate. Here, $10 \times 10 \mu\text{m}^2$ AFM height images from different sample positions are shown in a) - c) and g) - i) together with the corresponding Fast Fourier Transformations (FFT) in d) - f) and j) - l). The different motifs were obtained under fast drying conditions and can be related to different rotation angles between the hexagonal domains of the monolayers. As we cannot control the orientation of the first monolayer with respect to the second monolayer during the deposition process, all kind of Moiré motifs are formed during the sample preparation. The fast drying with the heatgun freezes the prevailing orientation of the monolayers right after the deposition and forces the second monolayer into the plane of the first one.⁵

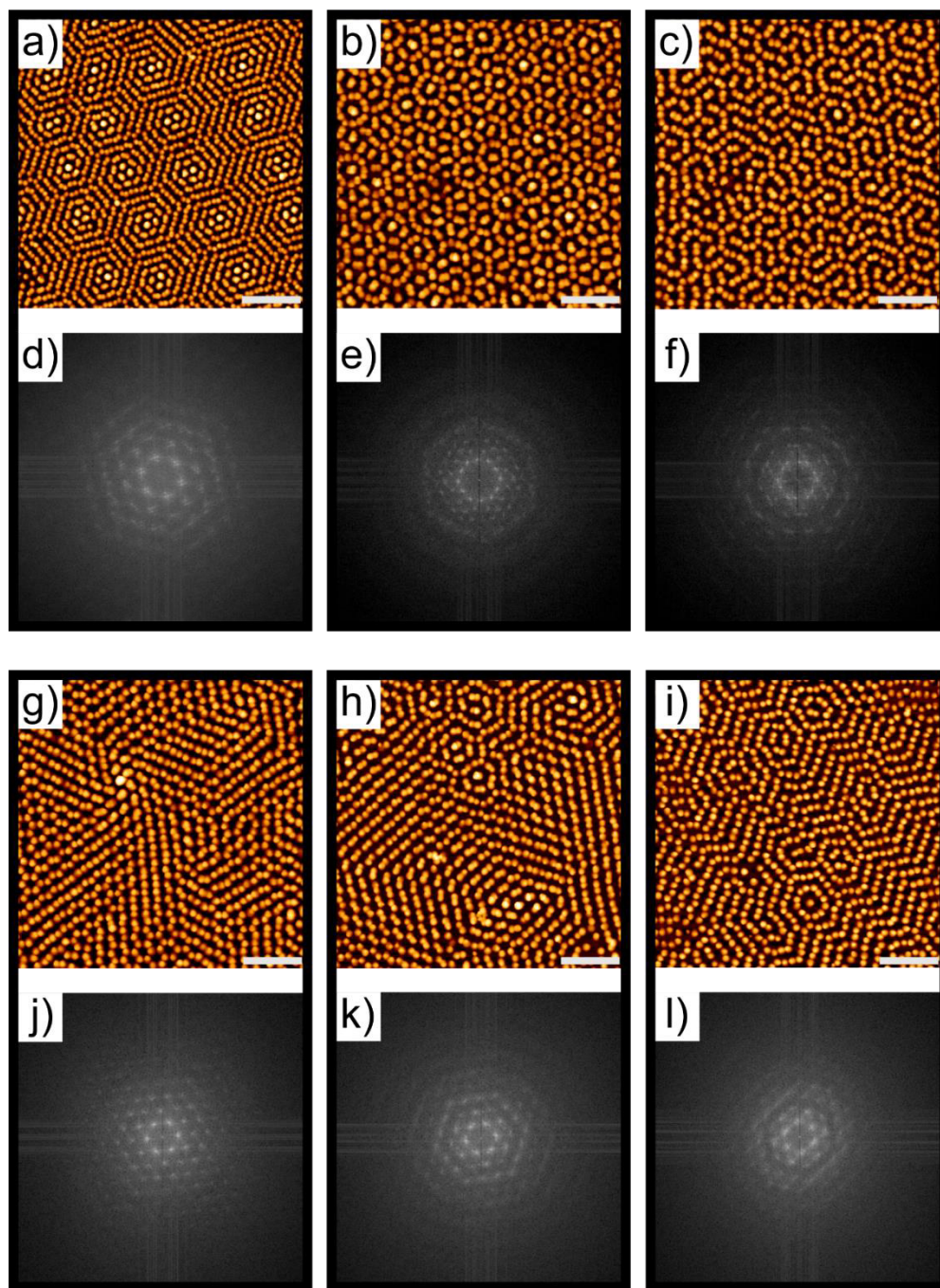


Figure S4. Moiré lattices obtained under fast drying conditions. a) – c) and g) - i) show AFM height images (scalebars correspond to 2 μm) with respective Fast Fourier Transformations in d) - f) and j) - l).

Honeycomb and Moiré structures at different sample positions

In Figure S5 magnifications of different positions within two large area AFM scans are shown for a honeycomb (a) and a Moiré (b) sample. The scans of the honeycomb sample all reveal honeycomb structures independent of the selected area. On the other hand, the Moiré lattices in (b) show different patterns depending on the sample position. The reason for this dependence can be explained by the multidomain nature of the hexagonally ordered sublattices from each of the sequential deposition steps. These finite size hexagonal domains have different

orientations towards each other and therefore have an impact on the final hc and especially the Moiré structures. In the latter case different rotation angles α are found throughout the whole macroscopic sample leading to local variations in the Moiré structure.⁵

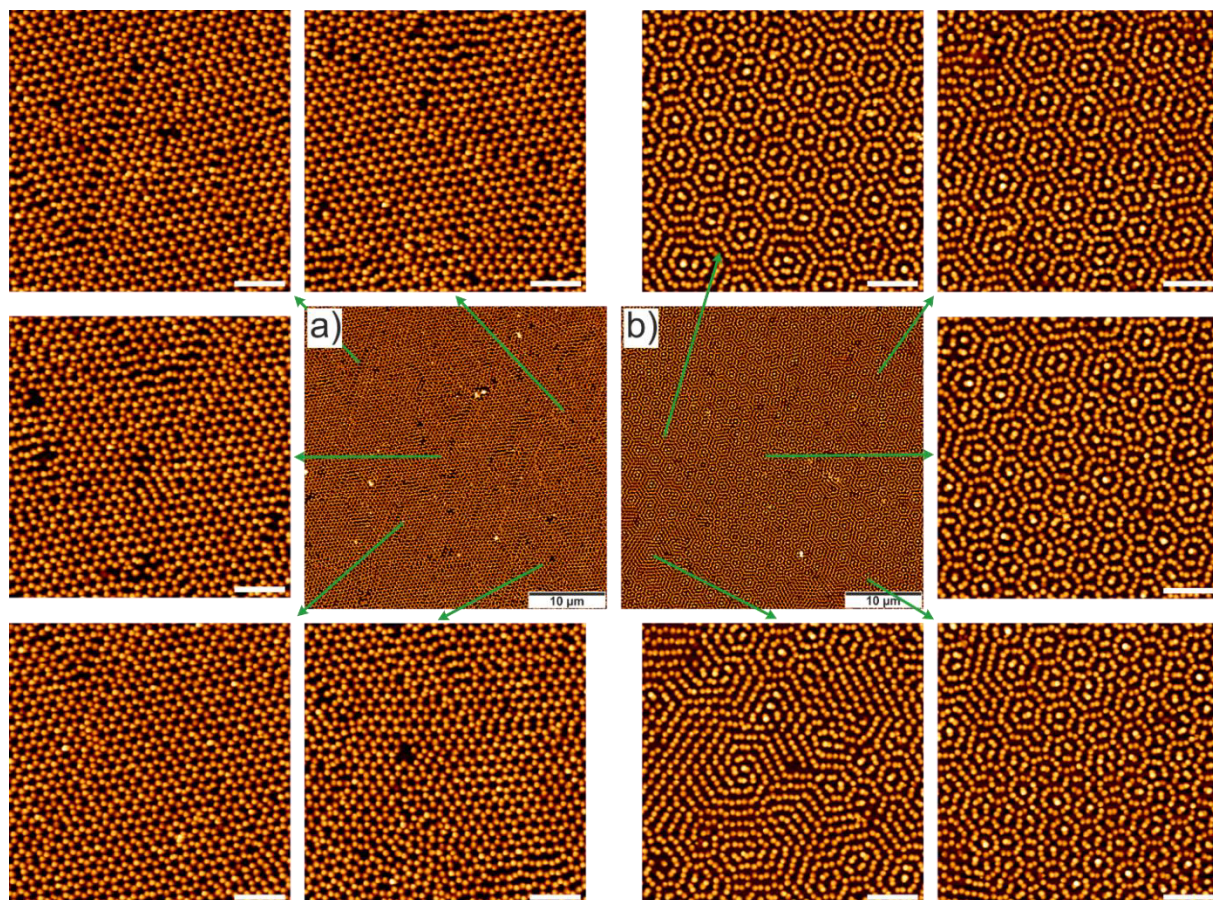


Figure S5. Structural analysis at different sample positions. AFM height images of a honeycomb (a) and a Moiré sample (b) with magnified images recorded at five different sample positions for each sample. The scalebars in the magnified images correspond to 2 μm .

FDTD simulations for finite and infinite sized lattices

Figure S6 compares results from FDTD simulations for finite and infinite sized honeycomb lattices (Ag-PNIPAM) with values of d_{c-c} ranging from 432 to 510 nm. The spectra for the finite lattices in a) display a pronounced plasmonic contribution (uncoupled) at approximately 500 nm together with SLRs that red-shift from 581 nm to 658 nm as d_{c-c} increases. The SLRs are relatively broad with increasing linewidth with increasing d_{c-c} . The total number of particles in the simulation box for the finite lattices is relatively small (see figure S6 c), domain size of 5) and electromagnetic coupling is restricted leading to weaker SLR intensities as compared to the purely plasmonic contributions at lower wavelengths. The only exception is the lattice with the smallest value of d_{c-c} (432 nm) where similar intensities are observed for the SLR and the purely plasmonic mode. In contrast the spectra of the infinite lattices in b) show much more

pronounced SLRs with significantly reduced linewidths. For these simulations periodic boundary conditions were used to effectively describe lattices with infinite numbers of particles. This leads to strong Bragg modes, which in turn result in pronounced SLRs especially for values of d_{c-c} between 432 and 469 nm.

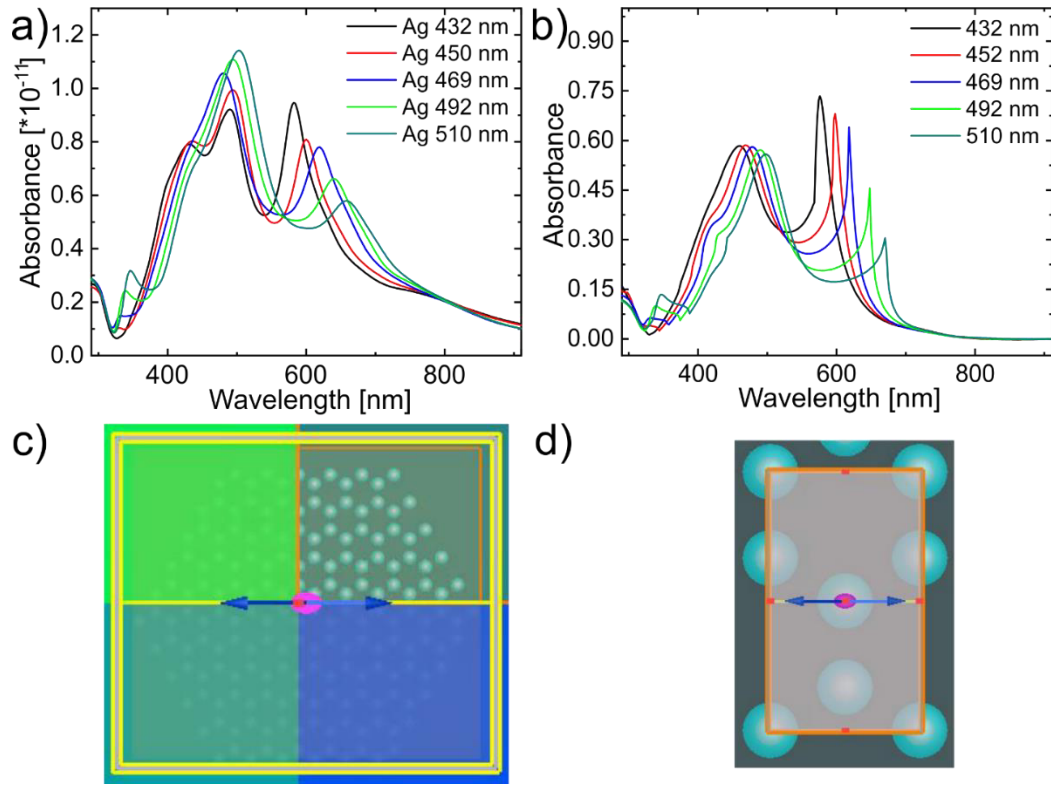


Figure S6. Simulated absorbance spectra of Ag-PNIPAM hc arrays with varying d_{c-c} from FDTD simulations using a finite sized lattice (domain size 5) (a) and using periodic boundary conditions creating an infinite sized lattice (b). Setup used for FDTD simulations for the finite (c) and the infinite lattice (d).

FDTD simulations for finite sized silver, gold and binary honeycomb arrays

Figure S7 shows calculated absorbance spectra for silver honeycomb lattices with increasing values of d_{c-c} from 432 (black trace) to 510 nm (blue trace) in a), for gold honeycomb lattices with increasing values of d_{c-c} from 455 (black trace) to 510 nm (red trace) in b) and for binary honeycomb lattices with increasing values of d_{c-c} from 445 (black trace) to 510 nm (green trace) in c). The calculated absorbance spectra correspond to the experimental spectra shown in the main manuscript in Figure 4a-c. Qualitatively the calculated and experimental spectra match very well. In addition, we find very good agreement between the SLR positions from experiment and simulation (see Table S1-3 for the SLR positions).

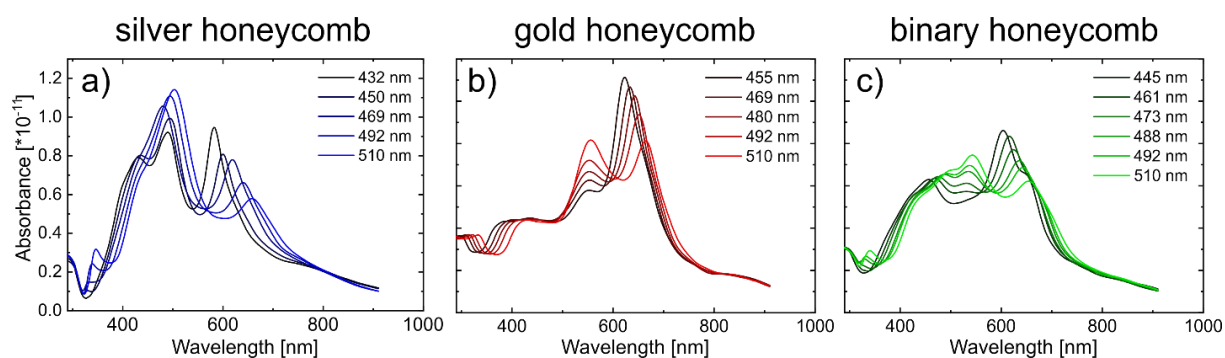


Figure S7. Influence of lattice period and plasmonic material. Calculated UV-vis absorbance spectra for Ag-PNIPAM (a), Au-PNIPAM (b) and binary nanoparticle honeycomb structures (c) from FDTD simulations.

Tables S1 to S3 list the SLR wavelengths of the different hc arrays from experiment and FDTD simulations in dependence of d_{c-c} . The values of d_{c-c} correspond to the nearest-neighbor center-to-center distances in the hexagonally ordered sublattices used in the double deposition process.

Table S1. SLR positions from experiment and simulation for Ag-PNIPAM hc arrays with varying d_{c-c} .

d_{c-c} [nm]	λ_{SLR} [nm] experiment	λ_{SLR} [nm] simulation
432	580	581
450	595	600
469	617	619
492	636	641
510	650	658

Table S2. SLR positions from experiment and simulation for Au-PNIPAM hc arrays with varying d_{c-c} .

d_{c-c} [nm]	λ_{SLR} [nm] experiment	λ_{SLR} [nm] simulation
455	614	623
469	622.5	633
480	630.5	643
492	643	651
510	658	665

Table S3. SLR positions from experiment and simulation for binary (Ag-PNIPAM + Au-PNIPAM) hc arrays with varying d_{c-c} .

d_{c-c} [nm]	λ_{SLR} [nm] experiment	λ_{SLR} [nm] simulation
445	594.5	604
461	610	616
473	620	624
488	631	636
492	638	642
510		656
518	658	

Near-field intensities from FDTD simulations of honeycomb lattices

Figure S8 shows near-field electromagnetic intensity ($|E/E_{inc}|^2$) maps from FDTD simulation of different honeycomb lattices with a fixed value of $d_{c-c} = 492$ nm. In the unary systems, maps at the LSPR positions of gold (a) and silver (c) show the excitation of dipolar resonances with some indication of near-field coupling between closest neighbors. The coupling is stronger for the silver particles as expected. In the binary system (layout for simulation shown in e), the map calculated at the LSPR of gold (f) shows dipolar excitations of both gold and silver particles. In that case the silver LSPR is still sufficiently excited at the resonance wavelength of the gold particles. Here again some weak near-field coupling between neighboring particles is visible. The map calculated at the LSPR of silver (g) shows dipolar excitations of mostly the silver particles and very weak excitation of the gold particles. In that case near-field coupling is not visible. For the unary and the binary system, maps calculated at the SLR position (b, d, h) reveal much stronger near-fields, strong coupling and the typical diffraction mode structure.

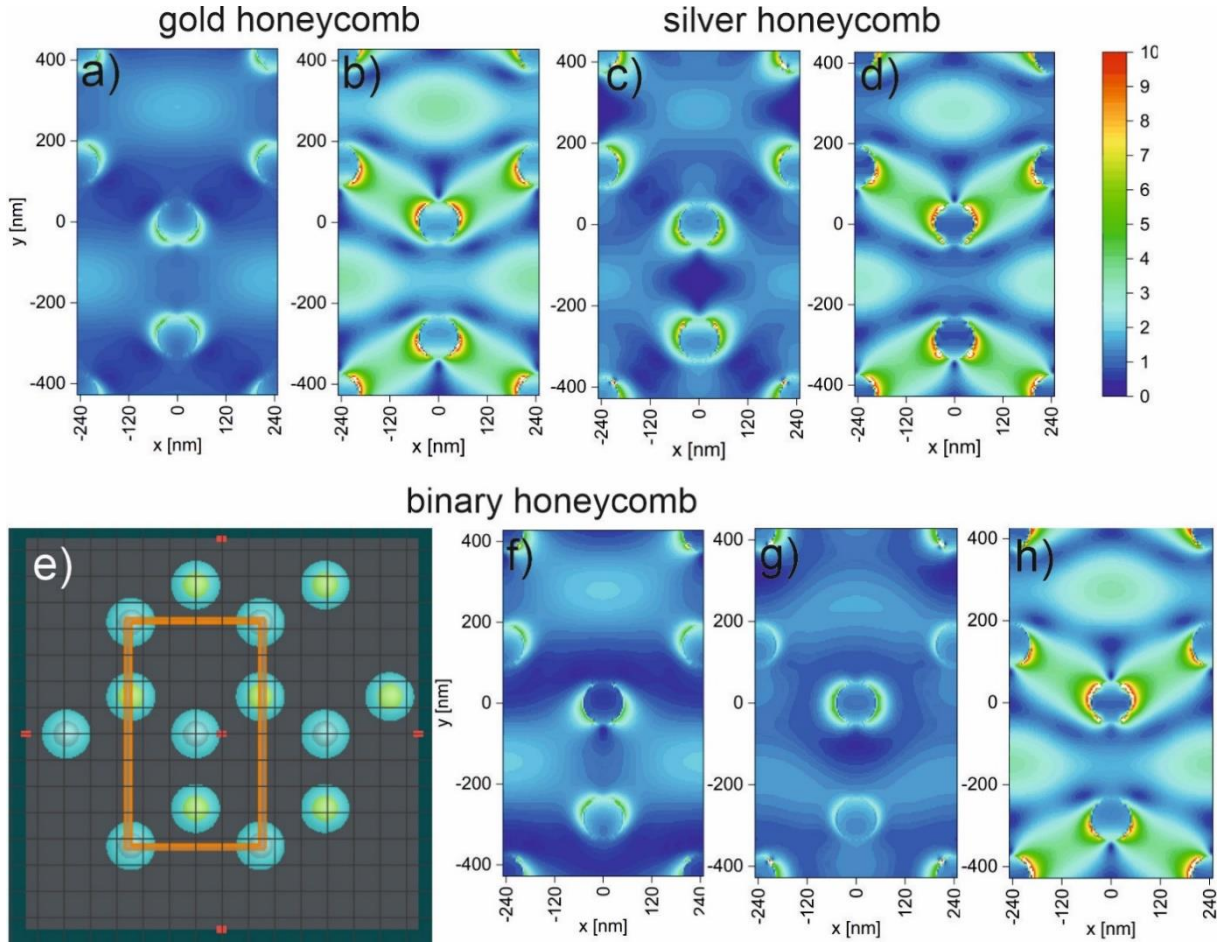


Figure S8. Near-field electromagnetic intensity maps from FDTD simulations of infinite sized gold (a, b), silver (c, d) and binary (f-h) honeycomb lattices with $d_{c-c} = 492$ nm. Maps were calculated at the LSPR positions for gold (a, f), silver (c, g) as well as at the SLR positions (b, d, h). The intensity scale is the same in all images. The simulation layout for the binary lattice with gold (yellow) and silver (grey) particles at alternating positions is shown in e).

FDTD calculations for silver and gold arrays with different lattice geometries

Figure S9 shows the effect of different lattice geometries on the optical response for simulated arrays with finite domain sizes for silver in a) and for gold in b). Confirming the experimental results, the hexagonal lattice (black trace) shows the most pronounced SLR when compared to the LSPR. The Moiré (blue trace) and hc (red) lattices possess almost the same absolute SLR peak intensity but the respective uncoupled plasmonic contribution at lower wavelength is much stronger. The positions of the SLRs match the experimental results nicely. The hexagonal lattice and the Moiré lattice possess almost the same resonance positions and only the SLR of hc lattice is clearly blue-shifted. This observation holds for the silver and the gold arrays.

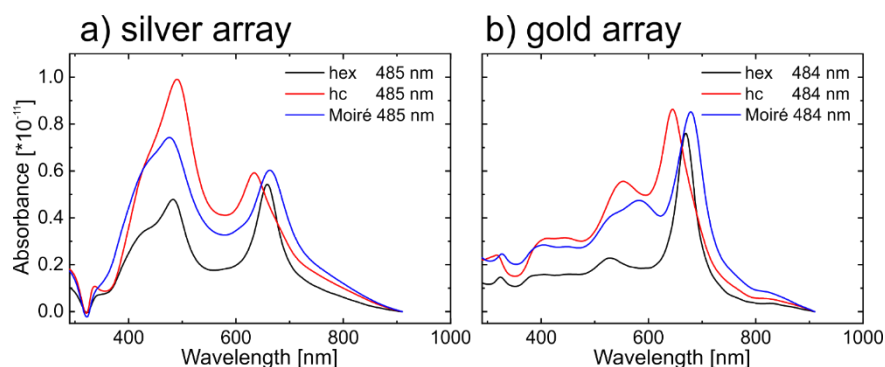


Figure S9. Influence of lattice geometry on optical response. Simulated UV-vis absorbance spectra of silver nanoparticles (a) and gold nanoparticles (b) in hexagonal (black trace), honeycomb (red trace) and Moiré arrays (blue trace).

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9 Outlook

This thesis contributes to the effort to find a cheap and easy alternative for lithographically prepared systems in the field of plasmonic and photonic applications. I studied and optimized the interface self-assembly of plasmonic silver and gold nanoparticles in PNIPAM polymer shells into hexagonal, Moiré and honeycomb structures. Moreover, I demonstrated the influence of interparticle distance on the LSPR and the SLR as well as the influence of refractive index environment, plasmonic material and size and lattice geometry. These findings were supported by simulation methods like CDA and FDTD.

Following this extensive study of the creation of surface lattice resonances in self-assembled nanoparticle monolayers and their comparison to lithographic examples, it is time to focus on possible applications. Such applications could be refractive index sensors¹, a SERS platform² and foremost, the eligibility as base for a plasmonic nanolaser.³ Up to now, self-assembled plasmonic surfaces were only applied in scientific prototypes. A large-scale application or even commercial application is not yet in sight. The high optical losses are still a major downside of the self-assembled systems. However, the robust SLRs with high Q factors presented in this thesis are one step towards application.

For example, for the preparation of nanolasers the addition of a gain medium into the direct environment of the plasmonic lattice is required.⁴⁻⁹ The gain medium can consist of a dye⁴⁻⁶ or quantum dots¹⁰, which possess a spectral overlap with the SLR. By excitation of the dye with an external laser energy is feed into the lattice mode until population inversions leads to the emission of a sharp lasing signal.⁴ The gain medium can either be applied as a static component embedded in a polymeric layer¹¹ or dynamically in a liquid layer inside a (micro)fluidic channel.¹² The advantage of a dynamic system would be the avoidance of bleaching of the dye and the possible switching between carrier liquids. Like this, the refractive index environment and therefore lasing wavelength could be tuned. The thermoresponsive films presented in this thesis could generate a similar tunability of the RI environment. A comparison to already existing works using lithographically prepared samples that successfully showed lasing, will reveal the potential of such self-assembled structures. It will shine light on the importance of structural perfection, particle quality as well as crystallinity, and whether self-assembled monolayers can already be used as basis for nanolasers.

After a general proof of concept, the system will profit from further optimization of the assembly parameters, core material or shape as well as interparticle distances. Inherently, self-assembly leads to point defects and grain boundaries that dramatically decrease the optical

mode quality. Thus, the development of a self-assembly method yielding large defect-free monolayers might prove to be detrimental for making self-assembled nanoparticle arrays a serious alternative for lithographically prepared devices. For this, a strong emphasis is currently put on the fundamental research on the interplay of the multiple forces playing a role during and after interface assembly.¹³⁻¹⁶ A recent study on silica-PNIPAM core/shell microgels showed significant changes in particle assembly geometry and order upon transfer from the air/liquid interface of a Langmuir trough to a glass substrate and the influence of the drying conditions.¹⁴ Small-angle light scattering reveals *in situ* a continuous decrease of interparticle distances upon compression of the monolayer, whereas upon transfer (*ex situ*) an “isostructural phase transition” from shell to shell contact to core to core contact is witnessed. Other works for example focus on the fabrication of self-assembled structures beyond hexagonal packing¹⁷ as well as chiral surface lattice resonances¹⁸⁻¹⁹. Moreover, a post-treatment of the assembled monolayers at the air/water interface such as ultrasonic treatment could help to reduce the defect density. In addition, the use of less lossy particle materials or monodisperse particles with a high crystallinity might lead to higher quality modes of the assemblies. Optimizing the main building blocks is an ongoing effort within the colloid community.²⁰⁻²² Finally, for the application in photonic devices, the preparation of large scale, low defect surfaces is not sufficient. To steer effectively light at the nanoscale, the surfaces have to be precisely positioned and structured on multiple length scales. For this, the possibilities of directed self-assembly have to be extended.

With the remaining obstacles regarding the optimization of the nanoparticle synthesis, the particle assembly and incorporation into functional devices the field of nanoplasmonics remains a challenging, exciting and promising field of study towards real-life applications.

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List of Conference Contributions

- (1) **Non-equilibrium assembly of plasmonic nanoparticles**
Oral Contribution, 11th Zsigmondy Colloquium, Bielefeld (2015)
- (2) **Periodic plasmonic arrays with controllable interparticle distances and plasmon resonance coupling**
Poster Contribution, 79. Jahrestagung der Deutschen Physikalischen Gesellschaft, Berlin, (2015)
- (3) **Surface lattice resonances in self-assembled colloidal monolayers**
Poster Contribution, International Conference on Self-Assembly in Confined Spaces, San Sebastián/Spain (2016)
- (4) **Colloidal plasmonic arrays exhibiting tunable surface lattice resonances**
Oral Contribution, 13th Zsigmondy Colloquium, Saarbrücken (2017)
- (5) **Tuning of surface lattice resonances in self-assembled colloidal monolayers**
Oral Contribution, European Materials Research Society - Spring Meeting, Strasburg/France (2017)
- (6) **Understanding and controlling surface lattice resonances in self-assembled plasmonic monolayer**
Poster Contribution, Particle-based Materials Symposium, Saarbrücken (2017)