

Mechanotunable Plasmonic Properties of Colloidal Assemblies

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Noble metal nanoparticles can absorb incident light very efficiently due to their ability to support localized surface plasmon resonances (LSPRs), collective oscillations of the free electron cloud. LSPRs lead to strong, nanoscale confinement of electromagnetic energy which facilitates applications in many fields including sensing, photonics, or catalysis. In these applications, damping of the LSPR caused by inter- and intraband transitions is a limiting factor due to the associated energy losses and line broadening. The losses and broad linewidth can be mitigated by arranging the particles into periodic lattices. Recent advances in particle synthesis, (self-)assembly, and fabrication techniques allow for the realization of collective coupling effects building on various particle sizes, geometries, and compositions. Beyond assemblies on static substrates, by assembling or printing on mechanically deformable surfaces a modulation of the lattice periodicity is possible. This enables significant alteration and tuning of the optical properties. This progress report focuses on this novel approach for tunable spectroscopic properties with a particular focus on low-cost and large-area fabrication techniques for functional plasmonic lattices. The report concludes with a discussion of the perspectives for expanding the mechanotunable colloidal concept to responsive structures and flexible devices.

1. Introduction

The surface electrons of noble metal nanoparticles can be resonantly excited to oscillations by light.^[1] The resulting localized surface plasmon resonance (LSPR) evokes intense colors, which are influenced by the size, shape, material, and dielectric environment of the colloidal particle.^[2] The resonant field

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enhancement and subdiffraction electromagnetic energy confinement has led to a variety of applications such as electrochromic smart windows,^[3] enhanced oxidation reactions,^[4] highly sensitive Raman scattering,^[5] energy transport below the diffraction limit,^[6] optically active cavities,^[7] and nonlinear optical processes.^[8] The use of plasmonic back reflectors^[9] in photovoltaic devices is of particular interest because they increase the conversion efficiency of inorganic^[10] as well as organic^[11] solar cells. The intrinsic absorption losses in metallic particles can be used in photothermal therapy, enabling localized heating.^[12] However, these losses are a bottleneck for the current development in plasmonic waveguiding and sensing applications which are limited by the associated broad linewidth.^[13] To take advantage of the plasmonic properties of the nanoparticles while reducing their losses for these applications, different approaches are required. In this context, surface lattice

resonances (SLRs) offer a possible solution. A plasmonic SLR occurs when the plasmonic nanoparticles' LSPRs couple to the diffractive Bragg modes.^[14] In consequence of this effect, excessive electrical fields arise on the surface, which are very sensitive toward changes of the lattice spacing and the dielectric surrounding.^[15] Since the first experimental realization in 2008 by the groups of Grigorenko^[16] and Barnes,^[17] plasmonic SLRs have been shown in a variety of applications such as ultranarrow band absorbers,^[18] nonlinear field enhancement,^[19] strong coupling to dyes,^[20] and engineering of nanolasers.^[21]

The current development in nanocrystal synthesis and colloidal self-assembly methods enables a colloidal approach toward the fabrication of arrays that feature SLRs with predetermined spectral properties. These colloidal selfassembly methods can be implemented for large areas and are water-based, making them environmentally friendly and low-cost.^[22,23] Readily available simulation techniques such as the coupled dipole approximation (CDA) or the finitedifference time-domain (FDTD) method can be used to determine the optical parameters and spectroscopic response that lead to the narrow spectral width (down to 1–2 nm) compared to the significantly broader resonances found for single plasmonic particles (>80 nm width).^[24] Such narrow linewidths were shown recently for lattices with gold^[15] and silver^[25]



nanoparticles. In the study of the Tamulevičius group,^[25] hexagonal lattices with self-assembled silver cuboctahedra were presented with quality factors (resonance wavelength divided by linewidth) of up to 80, as compared to typical LSPR values of about 10.^[14] The FDTD method is especially useful to calculate the response of plasmonic particles, as there is a wide range of geometries accessible through wet-chemical synthesis. For instance, spherical particles,^[26] anisotropic particles such as rods,^[27] hollow^[28] as well as multilayered core/shell particles^[29] can be achieved via scalable synthesis methods. In a periodic array of plasmonic particles, the lattice period, and thus the nearest-neighbor interparticle distance, crucially determines the plasmonic SLR properties, since pronounced SLRs require an energetic overlap between the single particle LSPR and the Bragg mode. This distance control can be achieved by core/shell particles where the shell functions as a dielectric spacer^[30] or by templates,^[31] which direct particles into arrays with predefined interparticle distances. Suitable templates can be obtained by using mechanical instabilities (wrinkling),^[32] by laser-interference lithography,^[33] or by softlithographic molding.^[15] The dielectric spacer materials, in turn, can be exchanged with functional or flexible materials such as electrochromic polymers^[34] or polydimethylsiloxane (PDMS)^[26] so that the assemblies become electrically or mechanically tunable. Considering the multitude of available polymers, this opens up a wide range of possibilities to harness collective plasmonic properties for the next generation of large-area flexible devices.

A mechanical deformation can be further utilized to comply with the aspired feedback, which is a central concept in the field of mechanochemistry.^[35] Here, the applied strain evokes molecular rearrangement or conformational changes, enabling a chemical response.^[36] In optical analogy, the deformation of plasmonic particle assemblies leads to changes in the lattice constant and the resulting plasmonic response. However, within this arising field of mechanoplasmonics,^[26] the practical demonstrations of colloid-based arrays featuring SLRs with tunable properties are still rare. A proof of concept was recently realized by the Odom group, using top-down lithographic methods.^[37] In a process combining photolithography, etching, electron-beam deposition, and lift-off on a PDMS substrate, they showed reversible tuning of the optical response by mechanical deformation. By incorporation of an organic dye, it was possible for the same group to use the flexible SLR substrate as optical feedback for a tunable laser.^[38]

In a similar fabrication process, the Halas group has investigated the color tunability during anisotropic stretching.^[39] These concepts and more are addressed in this progress report. The limitations in scalability, reproducibility, and functionality can be overcome through self-assembly strategies using wet-chemically synthesized nanoparticles. In the following sections, we discuss the physical properties of SLRs, their angle-dependent dispersion and optical changes during stretching. This theory part is followed by sections dealing with interface-mediated and template-assisted assembly as well as the anisotropic tunability of these colloidal assemblies. Finally, we extend the scalable colloidal assembly concepts to responsive and functional surfaces.





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2. Spectroscopic Properties of Tunable Plasmonic Lattices

Electromagnetic modeling provides a basis for both the choice of the colloidal building blocks as well as the desired assembly structures. Thus, we first introduce the basic concepts for spectral properties on the single particle as well as the assembly level along with the suitable modeling tools, which will enable the reader to establish a rational design approach.

Figure 1a shows the simulated extinction efficiency, *Q*, for a spherical gold particle with a diameter of 80 nm. Here, *Q* is defined as the extinction cross section divided by the area of the particle.^[40] The calculations were performed using a commercial numerical (FDTD) method. The particle exhibits a single, dipolar LSPR peak at a wavelength of 550 nm in air. However, in the case of 2D gratings, diffraction becomes evanescent to radiative (Rayleigh anomalies) at the wavelengths $\lambda = na$, where *n* is the refractive index of the surrounding medium and *a* is the lattice constant.^[41] Figure 1b shows the first and second-order Bragg diffraction from a 2D nanohole array written in PDMS with a varying lattice constant (*a* = 420, 440, 500 nm). In contrast to the plasmonic mode (Figure 1a), the line width of these photonic modes is comparably narrow.^[42]

The ordered arrays possess the combined properties of particle plasmons and diffractive modes (see Figure 1c), also known as plasmonic hybridization.^[43] At the SLR conditions



the incoming light is trapped inside the lattice plane and leads to a narrow full width at half maximum (FWHM or line width) and strongly enhanced local electric fields at the nanoparticle surface.^[38,42] This occurs due to the constructive interference and coherent coupling at the SLR position which leads to the standing wave formation and hence allows for localized field enhancement. A comparison of the normalized field strength is shown in the bottom of Figure 1 for three different cases: d) the single particle LSPR at 590 nm, e) the resonance at 550 nm (red marker in spectra), and f) the SLR at 650 nm (blue marker in spectra). It is evident that there is a threefold field enhancement in the case of the SLR as compared to the single particle LSPR. Optimized intensity, width, and location of the SLR features depend on the lattice period and thus interparticle separation, the size of the particles and their shape. Auguié et al. investigated two different regimes: In the first case, the diffraction mode is located on the lower wavelength side of the LSPR, which leads to weak radiative coupling and hence broader SLRs. In the second case, the diffraction is located on the longer wavelength side of the LSPR, which allows for very sharp and intense SLRs.^[17]

In terms of varying the extinction strength and coupling with different diffraction orders (DO), the geometry of the lattice becomes significant. Auguié et al. studied the plasmonic coupling of LSPRs to in-plane diffractive modes for periodic lattices with different geometries such as square, honeycomb, and



Figure 1. Spectroscopic properties of tunable plasmonic lattices. a) Simulated extinction efficiency (*Q*) of a single gold nanoparticle (80 nm in diameter) in air. b) Simulated extinction of the first order $\langle 0,1 \rangle$ and second order $\langle 1,1 \rangle$ diffraction from a square grating (nanohole array in PDMS) with 420, 440, and 500 nm periodicities. c) Simulated extinction spectra (unpolarized) of a 2D plasmonic lattice of gold nanoparticles with same the periodicities. Red and blue markers highlight the wavelengths corresponding to simulations in (e) and (f), respectively. d) Normalized electric field (*E*/*E*₀) plot for a single particle determined at the LSPR peak position. e) Field plot for a plasmonic lattice with 440 nm spacing received at the LSPR peak position (red marker in (c)). f) Field plot for the same plasmonic lattice received at the SLR peak position (blue marker in (c)). Adapted with permission.^[15] Copyright 2019, American Chemical Society.

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hexagonal lattices. They found that no specific lattice geometry has advantages over the other in terms of linewidth since all of them have high degrees of symmetry. In the case of rectangular arrangements, they claimed that the particle separation distance in the direction perpendicular to the incident electric field is important.^[44]

The group of Törmä further extended these findings with the addition of a Lieb lattice geometry. They have introduced a simple Dirac model to understand the importance of diffraction orders in different lattices.^[45] Here, it is noteworthy that the SLR also has a dispersive nature similar to gratings, which becomes important for coherent energy transfer to a gain material. Figure 2 shows the band diagram in case of transverse electric (TE) illumination for different lattice geometries for the case of in-plane SLRs. Different geometries are mostly dependent on their DOs and the orientations of the in-plane electric dipole of each nanoparticle. The radiative direction of the in-plane electric dipoles determines whether a specific DO can be excited or not. The only major difference between honeycomb and hexagonal lattice geometries is that the honeycomb array has a larger number of particles within one unit cell and hence features a higher extinction. Similarly, a Lieb lattice has

three times more particles within the unit cell than the square lattice and thus exhibits a higher extinction. In terms of advantages, a suitable lattice geometry can hold specific symmetries and coupling which can further be used in bandgap openings, Dirac points, and topological phases.^[45] These lattice geometries are promising candidates for lasing phenomena, which so far have been observed only in square and rectangular lattices.[46] In the case of transverse magnetic (TM), off-normal incidence one may excite the out-of-plane component of the dipole inside the plasmonic nanoparticle if its size is sufficiently large. Odom and co-workers have investigated the out-of-plane SLR in a 2D array of gold disks. They found that the SLR linewidth can be tuned through the height of the plasmonic building block.^[47] In order to reveal this, a minimum height of 35 nm is required in the z-direction.^[24] The same group further investigated the dispersive nature of out-of-plane lattice plasmon modes (OLPs). They suggested that delocalized OLPs are a kind of surface Bloch mode. As the OLP dispersion evolves from a stationary state to a propagating state, the nonradiative loss decreases because of weak local field confinement, whereas the radiative loss increases because of strong coupling to the leaky zeroorder harmonic.^[48] In the case of out-of-plane excitation, the



Figure 2. Diffraction effects from different lattice geometries. a–c) Top: scanning electron microscopy (SEM) images of square, honeycomb, and Lieb lattice arrays. Bottom: calculated photon energy and diffraction orders (DOs) for transverse electric (TE) polarized light of the respective lattices. Reproduced with permission.^[45] Copyright 2017, American Physical Society.

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lattice geometry contributes significantly since stronger coupling occurs in all directions within the plane of the array, as studied by the group of Boyd.^[49]

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The dielectric environment plays an important role in the design of plasmonic lattices. The difference between the index of the substrate and the surrounding medium leads to an asymmetry that strongly hinders the radiative coupling between particles.^[17] For an index-matched case, a single SLR with high quality (superior signal to noise ratio) is expected but it hinders the application aspect such as biosensing and plasmon lasing, where index matching is often incompatible with the sensing situation.^[50,51] Auguié et al. investigated that the presence of a homogeneous environment is indeed a "soft" condition to observe SLRs at normal incidence.^[17] It can be easily relaxed for off-normal incidence where SLRs can be excited for an inhomogeneous environment as well. They further explored the symmetry problem in a detailed theoretical investigation. It was found that the excitation of SLRs under normal incidence is facilitated by the placement of metal nanoparticles into a symmetric environment, for example, by adding index-matching fluids in order to remove the refractive index contrast between the substrate and the surrounding medium. Using rigorous electromagnetic simulations, they showed that an asymmetric environment can suppress long-range interactions between the particles and thus inhibits lattice resonances for normal incidence. It was shown that the refractive index contrast and the distance of the array from the interface are the key parameters that determine the strength of diffractive coupling. The requirement of a homogeneous surrounding index also does not hold for out-of-plane lattice modes. The excited electric fields associated with neighboring particles are localized in the surrounding medium and the index mismatch between substrate and the medium is no longer critical. Similar results were provided by Tamulevičius and co-workers who studied the in-plane and outof-plane SLRs of hexagonal silver cuboctahedra assemblies.^[25]

To achieve a mechanotunable platform featuring high-quality SLRs via colloidal assemblies, some key parameters need to be considered: 1) The choice of the substrate material (Poisson's ratio) is crucial in terms of its tensile strength and hence flexibility. 2) The material and size of the colloidal building blocks should result in a suitable scattering contribution in the desired wavelength regime. 3) The interparticle distances and lattice geometries need to be optimized for efficient conversion of the excitation energy. More particles arranged into the lattice lead to narrower SLRs, with the theoretically best case being an infinite number of ordered particles. 4) Hence, defect-free colloidal assemblies on a large scale open up possibilities for a frontier technique to produce such kind of functional plasmonic surfaces.

3. Plasmonic Lattices via Colloidal Assembly

Coupling of single particle LSPRs with diffractive modes to form narrow bandwidth SLRs requires the arrangement of plasmonic nanoparticles into periodic lattices. Ideally, such lattices possess macroscopic dimensions with large single-crystalline domains. Here, self-assembly approaches are well-suited as they allow for the low-cost and often low-tech fabrication of ordered superstructures of particle-based building blocks on macroscopic areas. Countless self-assembly strategies were introduced in the last decades of which a few are ideal for the efficient and controlled preparation of periodic plasmonic lattices.

3.1. Interface-Mediated Assembly

A very promising approach to achieve periodic superstructures of plasmonic particles is interface-mediated assembly. This assembly method builds upon two general prerequisites: 1) The ability of colloidal particles to strongly adsorb to interfaces. 2) The lateral mobility of the particles at the interface, allowing for self-assembly into minimum free-energy structures. To meet these criteria, interface-mediated assembly typically utilizes liquid/liquid or air/liquid interfaces.

The assembly of solid particles on liquid/liquid interfaces has already been observed more than a century ago in stabilized emulsions of immiscible liquids, so-called Pickering emulsions.^[52,53] However, a theoretical explanation of the phenomenon has not been provided until about 70 years later, when the relation between the interfacial tension and the particle radius to the difference in free energy was derived^[54]

$$\Delta E = -\frac{\pi r^2}{\gamma_{\text{O/W}}} \left[\gamma_{\text{O/W}} - \left(\gamma_{\text{P/W}} - \gamma_{\text{P/O}} \right) \right]^2 \tag{1}$$

This equation provides the relation between the difference in free energy ΔE , the particle radius *r*, and the surface tensions γ between immiscible phases, represented here by oil (O) and water (W) as well as between the colloidal particles (P) and the respective liquid phases. For particles in the colloidal size range, the decrease in free energy is comparable to the thermal energy ($k_{\rm B}T$), leading to a thermally driven exchange of particles at the interface with a rate depending on the particle size. Larger colloidal particles, with a larger gain in free energy, adsorb stronger to the interface.^[55]

Adsorbed at the interface, colloids are subject to long-range attractive and short-range repulsive interparticle interactions. The interplay between these leads to the formation of ordered hexagonal lattices that can subsequently be transferred onto solid supports.^[56,57] At liquid/liquid interfaces, the repulsive interactions typically outweigh the attractive ones, resulting in non-close-packed layers of particles.^[58–61] At air/liquid interfaces, on the other hand, the attractive interactions, notably capillary forces, are typically dominating and lead to close-packed arrays.^[61,62] While hexagonal particle assemblies are the most frequently obtained structures from interface-assisted assembly, Hummel et al. have recently shown that any of the possible 2D Bravais lattices can be realized.^[63] This was achieved by adjusting the contact angle of the solid substrate that is used for the transfer of the particle monolayer from the interface.

A key challenge with respect to plasmonic monolayers that feature plasmonic/diffractive coupling lies in the required interparticle distances which are typically several times larger than the plasmonic particle diameter.^[41] Ideal colloids that can meet this requirement are core/shell particles that consist of a plasmonic nanoparticle core and soft polymer shells with large thicknesses. Thick polymer shells can be realized by seeded



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precipitation polymerization yielding hydrogel encapsulated nanoparticles with high colloidal stability.^[64] This route allows varying the shell thickness over a broad range, up to several hundreds of nanometers. Vogel et al. have shown that such hybrid colloids can be assembled at air/water interfaces leading to non-close-packed monolayers of the plasmonic nanoparticle cores with interparticle distances that depend on the thickness and compression state of the hydrogel shells.^[65] Using compression in a Langmuir trough, lattices with a wide range of interparticle distances became accessible due to the deformability of the soft shells. Similar to this work, Honold et al. have shown that attractive interparticle interactions present at air/water interfaces can be used to create freely floating monolayers of plasmonic core/shell colloids.[66] These monolayers were successfully prepared from a series of core/shell particles with differently sized gold and silver nanoparticle cores. Transfer from the air/water interface onto glass substrates was used to produce periodic plasmonic monolayers with interparticle distances that are defined by the shell size and plasmonic properties that depend on the core material and size. In contrast to monolayers of rigid particles prepared by a very similar approach,^[67] Volk et al. have shown that the dwell time of the core/shell particles at the air/water interface dictates the interparticle distance in the final particle lattice (see Figure 3).^[68] While monolayers that were withdrawn immediately after adsorption to the air/water interface possess interparticle distances that match closely the bulk hydrodynamic dimensions of the colloids (see Figure 3b), monolayers withdrawn at later times show significantly increased distances (see Figure 3c/d).

This time dependence of the lattice spacing is the result of lateral hydrogel shell deformation driven by interfacial tension. Consequently, it is possible to create periodic plasmonic monolayers with a broad range of periodicities from the same batch of core/shell particles by simply varying the dwell time at the air/water interface. This makes interface-mediated selfassembly of hard-core/soft-shell colloids a very powerful technique for the preparation of plasmonic coatings with tailored optical properties.

In more recent publications, Volk et al. have further shown that coating such plasmonic arrays with a polymer layer to match the refractive index of the glass substrate and thereby homogenizing the refractive index environment of the particles (see Figure 3e) has led to coupling between LSPR modes and diffractive modes featured as narrow bandwidth SLRs.^[30,69]

Furthermore, using the same approach of interface-mediated assembly for core/shell particles, it has been demonstrated that more complex lattice geometries are accessible. By repeating the transfer process of a free-floating particle monolayer from the air/water interface onto a substrate that already carries a first particle layer, new geometries arise as the second particle array settles into the gaps of the first one. Due to the deformable nature of the core/shell particles, this process still results in real 2D monolayers, i.e., all particles sit in the same lattice plane. Honold et al. have demonstrated that this method can be used to create binary honeycomb arrays consisting of plasmonic silver and gold nanoparticles at alternating positions.^[70] Recently, Volk et al. have expanded this approach and demonstrated that the drying conditions of the second monolayer on



Figure 3. Preparation of monolayers via interface-mediated assembly. a) Schematic depiction of the process for fabricating self-assembled monolayers at an air/water interface and the subsequent transfer onto solid substrates after certain dwell times. b–d) $10 \times 10 \mu m^2$ AFM height profile images of monolayers of plasmonic core/shell particles on glass substrates that were withdrawn from the air/water interface after different dwell times. Dwell time and center-to-center distance increases from (b) to (d) with distances of 359 ± 29 , 444 ± 34 , and 527 ± 28 nm. The insets show digital photographs of the corresponding coated glass slides. e) SEM side-view image of core/shell particles coated with an index-matching polymer layer. (a,e) Adapted with permission.^[68] Copyright 2017, Wiley VCH. (b–d) Adapted with permission.^[68] Copyright 2015, Wiley-VCH.





top of the first, substrate-supported monolayer determine the resulting monolayer structure.^[71] Slow drying leads to the previously observed honeycomb lattices (**Figure 4**a) while fast drying resulted in different Moiré lattices (Figure 4b/c), depending on the rotation angle between the arrays. They have further provided Brownian dynamics simulations, showing that the Moiré arrays correspond to a nonequilibrium deposition, while the honeycomb arrays correspond to the equilibrium case. In both cases, very good agreement between the simulated and experimental structures was found (Figure 4d–f).

A related approach for the formation of plasmonic structures is the use of self-assembled particles as a removable mask for metal deposition. This type of colloidal lithography has been shown to be capable of forming various plasmonic structures over large areas, ranging from simple triangles^[72] to crescents with tunable chirality.^[73] Among these structures accessible by colloidal lithography are also periodic nanohole arrays, also referred to as nanomeshes. These nanohole arrays can support SLRs and are typically fabricated by transferring hexagonally ordered arrays of polystyrene particles from an air/water interface onto substrates, followed by etching of the particles before depositing the metal. Stelling et al. have systematically examined such silver nanomeshes regarding their plasmonic properties by varying the particle sizes and thereby the size of the holes over a broad range and supporting their results with FDTD simulations.^[74] In a more recent publication, Torrisi et al. have shown an application for these nanomeshes as an intralayer film between transparent conductive oxides (TCO). They reported high transparency in the red to near-infrared spectral range in combination with high electrical conductivity, thus showcasing the viability of this type of material for applications such as smart windows or photovoltaic devices.^[75]

3.2. Template-Assisted Assembly

The introduced interface-mediated assembly method is a powerful tool for creating hexagonally ordered arrays. Additionally, the stacking of these arrays further extends the range of accessible structures to more advanced ones like honeycomb or Moiré lattices. Furthermore, interface-mediated assembly can be used to create masks for metal deposition. However, while



Figure 4. Comparison of the experimentally observed particle arrays to their theoretical counterparts. a) AFM image of an experimentally obtained honeycomb structure obtained by slow drying of a second layer of particles on top of the first one. b,c) AFM images of experimentally obtained Moiré structures obtained by fast drying of a second layer of particles on top of the first one. The scale bars in all three AFM images correspond to 2 μ m. d–f) Corresponding particle arrays from Brownian dynamics simulations. d) Honeycomb lattice matching the experimental result in (a). e/f) Corresponding theoretical lattices to (b) and (c), resulting from an overlap of two hexagonal lattices at respective angles of $\alpha = 11^{\circ}$ and 26° between lattices. Adapted with permission.^[71] Copyright 2019, Royal Society of Chemistry.

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these methods provide a simple method for large-scale assemblies, they are also limited by their underlying reliance on hexagonally ordered particles. Assemblies with a broader range of symmetries, more pronounced anisotropy, or local variation of the packing can be achieved via template-assisted self-assembly (TASA).^[31] Colloidal self-assembly is a thermodynamically driven process resulting from the interplay of different attractive interactions (e.g., van der Waals forces, Coulomb attraction, and depletion forces) and repulsive interactions (e.g., Coulomb and steric repulsion). Local energetic minima can be introduced by applying templates featuring attractive electrostatic interactions or support-capillary interactions that direct the particles during the drying process. To reach these minima, external driving forces can be applied via confinement, convective flow, electric/magnetic fields, or templating molecules (DNA). This technique is known as directed self-assembly and leads to particle deposition in a desired fashion.^[56,76,77] This section will discuss selected methods for TASA to create: 1) particle chains via evaporation methods, 2) square lattices via capillarityassisted self-assembly, and 3) customizable arrays via charge interactions. Such arrays of plasmonic particles are of special interest for: 1) optical waveguiding, 2) as a model system for mechanotunable lattice resonances, and 3) tailored design of optical bandgaps.

Drop-casting and spin-coating are well-known methods from thin-film preparation: A dissolved substance is deposited on a substrate by controlled evaporation of the solvent. This approach is also applicable for nanoparticle dispersions, resulting in the formation of close-packed particle monolayers, for instance.^[78,79] The spin-coating process is influenced by a variety of interaction forces determining the deposition step. In dispersion, colloidally stable particles exhibit electrostatic and/ or steric repulsion depending on their surface functionalization. During the drying process, the particles get confined in a thin liquid film in which capillary forces act between them. This interplay of attractive forces and repulsive interactions defines the resulting packing while the number of particles per area defines whether a sub-monolayer, a monolayer, or multilayers are formed. This layer formation is not only determined



by the stock particle concentration and the wetting behavior on the substrate but also by the rotation speed, as the centrifugal forces influence the initial liquid film thickness.^[80]

Exchanging flat substrates for topographically structured templates gives access to particle arrays with a wide range of possible array geometries. In general, any nanostructured substrate—no matter whether fabricated via e-beam-,^[81] interference-,^[15] or soft lithography^[82]—is applicable for TASA. A simple and lithography-free method for creating templates is controlled surface wrinkling.^[83] Such structures are fabricated by the deposition of a stiff material layer on top of an elastomer. As shown in **Figure 5**a, plasma treatment of PDMS results in the formation of a thin glassy layer with increased rigidity. The stiffness and thickness of this layer determine the wavelength and amplitude of the resulting sinusoidal wrinkles upon release.^[84,85]

The spin-coating process is significantly altered by the presence of surface wrinkles. In the drying step, the varying liquid film thickness leads to confinement of the particles inside the wrinkles (see Figure 5b). The capillary forces acting during further drying result in the formation of close-packed particle chains. Depending on the topography, namely, the amplitude and wavelength of the wrinkle, single or double lines are achieved as displayed in Figure 5c.^[32]

The template-assisted approach can be further adapted in analogy to drop-casting. In this case, the nanostructured template does not serve as the substrate but is used to confine the particle dispersion in between the template and a flat surface (e.g., glass). During the evaporation process, the particles replicate the topographic features in accordance with the confinement. By applying colloids with hydrophilic functionalities featuring attractive interactions with the substrate, it has been shown that various geometries like pyramids,^[82] lines,^[86] cylinders, and donuts^[87] can be reproduced with this method.

The template-assisted methods discussed before are suitable for the realization of long-range ordered particle arrays. However, there are limitations regarding the preparation of single particle arrays. These can be overcome by utilizing assembly methods that allow for more control over the deposition step.



Figure 5. Template-assisted assembly on wrinkled surfaces. a) Schematic illustration of the preparation procedure for sinusoidal wrinkles by oxygen plasma treatment of stretched PDMS. b) Scheme of the particle assembly into linear structures via spin-coating. c) SEM images (left) and respective photographs (right) of gold nanoparticle lines prepared in wrinkles with different periodicities. Adapted with permission.^[32] Copyright 2014, American Chemical Society.





Capillarity-assisted particle assembly (CAPA)^[88] utilizes a combination of pinning effects at the topographic features and convective particle flow for achieving such control.

The mechanism of particle assembly through drying of particle dispersions on flat substrates has been studied intensely by the group of Nagayama^[89,90] It was found that the increased solvent evaporation close to the three-phase contact line induces a convective flow of particles toward the contact line. This phenomenon is often referred to as the "coffee ring effect" and can be utilized for particle assembly. The assembly processes based on convective flow have been foremost interpreted by Wolf and co-workers^[91,92] who refined the common dip-coating process. As shown in Figure 6a (center right), a droplet containing dispersed particles is confined between the template and a glass slide. Nanoparticles accumulate at the meniscus as a result of the convective flow. By withdrawing the template, the meniscus is moved across the substrate leading to particle deposition in the grooves of the template. The parameters to control in these experiments are predominantly the movement speed, the substrate wetting (by surfactants), and the dew point. Two cases are distinguished for the assembly: the convective and the capillary regime. The convective assembly occurs at very low contact angles (<20°) in which the particles are predominantly confined by a remaining thin solvent layer.^[91] This film forces them into the recesses during the evaporation, similar to the mechanism during spin-coating. Conversely, the capillary regime describes the assembly at comparably high contact angles (>20°). The meniscus is not continuously moving but pinning at the topographical features. As a result, capillary forces drag particles into the recesses where they stay confined

after unpinning. By rational design of the features, the orientation of anisotropic particles can be predefined. For instance, an energetic minimum can be reached by nanorods aligning parallel in rectangular grooves.^[81] By directing particles into accurate positions, this tightly controlled method also enables the deposition of single particles in an array.^[93] The technique is applicable to various types of topographically structured templates, including elastomeric substrates.^[94] Thus, it is an excellent foundation for the preparation of mechanotunable colloidal assemblies.

Suitable templates for colloidal assembly can be prepared by various methods of which we want to highlight laser interference lithography (LIL).^[95] Figure 6a depicts the use of LIL in combination with CAPA to produce a plasmonic lattice. Gupta et al. employed LIL to produce large-scale structures with nanometer precision at low cost as compared to e-beam lithography. Lloyd's mirror technique was used where a single coherent laser beam is converted into two coherent sources. Interference of the two beams occurred on a photosensitive material. By a second exposure with 90° rotation, a nanopillar structure was formed after curing (see Figure 6, blue frames). This master was replicated into a nanohole structure using PDMS (red frames). With this template, 80 nm diameter gold spheres were assembled in a square lattice of single nanoparticles as displayed by the black frames.

Aside from self-assembly methods based on evaporation, there are other methods that direct colloidal particles into defined geometries. For example, electrostatic interactions between charged nanoparticles and templates are applicable to create plasmonic particle arrays. These interactions can be



Figure 6. Capillarity-assisted particle assembly with soft-lithography templates. a) Scheme representing the fabrication of a stretchable 2D lattice using a combination of laser interference lithography with double exposure, soft molding with PDMS, and directed self-assembly of plasmonic nanoparticles. b) SEM images of the fabricated nanopillar master, its PDMS mold, and the 2D plasmonic lattice. Adapted with permission.^[15] Copyright 2019, American Chemical Society.





triggered either by inducing charges chemically or electrically. The former of these methods requires chemical functionalization of the particles and the template. The latter assembles functionalized particles from a conductive medium on conductive templates. Realization of assembly via chemical interaction requires comparably low experimental effort with moderate control of the process. There are different ways to achieve chemical surface structuring based on microcontact printing or lithographic methods. Microcontact printing is an appealing method as it does not require specialized equipment. Hammond and co-workers have applied PDMS stamps from replica molding to print polyelectrolytes on top of a substrate.^[96] Depending on the pretreatment of the PDMS stamp, different printing patterns can be realized with a simple pillar structure. By changing the wettability, circles, rings, and dots could be printed. Using substrates with polyelectrolyte multilayers for the printing results in a charge contrast which induces selective attraction of charged colloidal particles by just immersing the templates in a dispersion (see Figure 7a).

The resolution with respect to the applicable feature size could be improved further by using lithographic templates since plasmonic colloids usually demand geometries in the nanometer regime for proper assembly. The group of Mulvaney utilized e-beam lithography to create spaced patterns with feature sizes of 80–300 nm. These wells were postmodified by silanization with amines.^[97] The resulting attractive interactions

between the amine groups and the surface of gold nanoparticles enabled assembly of plasmonic particles by simple immersion into a colloidal dispersion. Due to the sufficiently small features, the deposition of either small clusters or single particles could be obtained.

The application of conductive substrates like nanostructured ITO enables further possibilities to assemble particles via charge interactions. Electrophoretic particle deposition (EPD) has been introduced as a tightly controlled method for single particle deposition that facilitates the orientation of anisotropic particles.^[98] Figure 7c depicts an electrophoretic cell used for the particle deposition. Applying a voltage to a colloidal dispersion leads to an attraction of the gold particles (functionalized with positively charged polyelectrolyte) by the negatively charged electrode. The dielectric PMMA coating screens the charges of the electrode which leads to selective deposition in the uncoated areas. Compared to chemical methods, this process is more complex to apply but delivers direct control of the assembly through the electrolyte concentration and applied voltage. Utilization of anisotropic wells with similar particles like rods, for instance, results in further control on the orientation of particles. By that, the intrinsic polarization dependence of such plasmonic particles could be translated to the response of the array. Yet, EPD has not been shown on flexible substrates. However, this could be easily achieved via evaporation of thin metal layers^[99] or by conducting a wet transfer step of the assembled particles.^[32]



Figure 7. Particle assembly via electrostatic interactions. a) Schematic of microcontact printed polyelectrolyte multilayers (top) and optical microscopy of polystyrene particles assembled on such printed substrates (bottom). b) Depiction of particle assembly by immersion of a nanostructured amine-functionalized glass in a colloidal gold dispersion. c) Schematic of electrophoretic particle assembly on nanostructured ITO. d) SEM image of the resulting single particle assembly on ITO (Scale bar: 2 μ m). (a) Reproduced with permission.^[96] Copyright 2002, American Chemical Society. (b) Reproduced with permission.^[97] Copyright 2018, American Chemical Society. (c,d) Reproduced with permission.^[98] Copyright 2018, American Chemical Society.

Different assembly methods have been introduced to

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achieve defined particle arrangements. Except for e-beam templating, these methods share comparably low experimental effort and good scalability. This makes them especially suitable for large-scale applications and mechanotunable plasmonics.

4. Mechanotunable Plasmonic Systems

The optical response of periodic plasmonic particle arrays depends strongly on the lattice geometry and its periodicity. Thus, modulation of the interparticle distances via changing the lattice constant as well as the lattice structure allows for tuning of the optical properties by influencing near-field and/ or far-field electromagnetic coupling. Mechanical strain is a straightforward and easily applicable method to achieve in situ tuning of the particle distances. Two boundary cases can be distinguished for such deformation: the isotropic strain leading to a uniform increase of all interparticle distances and the uniaxial strain

Different scenarios for the structural response upon uniaxial strain are introduced in Figure 8.

For elastomers, a deformation is typically accompanied by a transversal contraction (Poisson's ratio > 0) which leads to an increase of the interparticle distance (a) along the stretching axis and a perpendicular reduction of the distance (b).^[100] This effect can be utilized to create changes in the near-field coupling of nonperiodic structures, for instance (see Figure 8a). Hereby, a polarization-dependent optical response is generated. Deformation of 1D-periodic structures may further result in the tuning of optical waveguiding or perpendicular lattice coupling (see Figure 8b). 2D-periodic structures as shown in Figure 8b intrinsically feature polarization-dependent optical properties based on SLRs. More complex modulations could be achieved by using different matrix materials. For instance, colloidal membranes featuring pressure-sensitive molecular interactions would lead to nonlinear transitions.^[101]

In general, a mechanical strain enables the transition of the array geometry and its lattice modes thereby which will be covered in the following sections.

4.1. Tuning of Interparticle Coupling

For achieving mechanotunable optical properties, several requirements must be fulfilled: First, the optical feedback of the plasmonic particles needs to be maintained. Namely, the structures have to be exposed at the surface, or the substrate has to be transparent. Second, the substrate needs to be deformable. Ideally, it is an elastomer since this guarantees intrinsic reversibility of the tuning process. Bürgi and co-workers have demonstrated a facile method to create such mechanotunable plasmonic structures by coating of PDMS with spherical gold nanoparticles.^[102] PDMS is a transparent elastomer with a Poisson's ratio close to 0.5, meaning that there is no volume change upon stretching. This, combined with possible deformations over 150%, renders PDMS to an ideal substrate for mechanotunable optical materials.^[103] In the case of randomly adsorbed gold spheres, stretching led to a change in interparticle spacing. As shown in Figure 9a, the strain in x-direction induces an increased spacing along that axis while the transverse strain decreases the spacing along the y-axis. This is accompanied by a color transition from purple to blue as shown in the photograph. The effect can be explained by arising interparticle coupling as a consequence of the decreased spacing in y-direction. The extinction spectra that are shown in Figure 9b reveal a redshift of the absorbance maximum with an increasing strain related to near-field resonance coupling.^[104,105] The asymmetric peak results from a superposition of the coupling mode (excited by light polarized in the y-direction) and the uncoupled dipolar mode in the x-direction. This simple example shows that mechanoplasmonic tuning is achievable via facile methods. Yet, it features a polarization-dependent optical response which is of interest for strain sensing^[26] and color tuning.^[39]



Figure 8. Substrate deformation upon uniaxial deformation depending on the array periodicity. a) For unordered particles. b) For a 1D-periodic lattice arranged along the strain direction. c) For a 2D-periodic lattice with symmetry axes parallel and perpendicular to the strain direction.







Figure 9. Mechanotunable plasmonic response. a) Left: schematic of particle behavior on PDMS under uniaxial strain. Right: photograph of the respective sample at rest (top) and under strain (bottom). c) Particle lines on PDMS under x% strain showing chain fragmentation. d) Respective UV-vis spectra between 0% and 50% strain. e) LSPR peak position over multiple cycles. (a,b) Reproduced with permission.^[102] Copyright 2014, Royal Society of Chemistry. (c-e) Adapted with permission.^[26] Copyright 2017, American Chemical Society.

For the realization of inverse tuning (spectroscopic blueshift upon stretching), further requirements have to be met which cannot be delivered via random particle deposition. It is necessary that particles are plasmonically coupled along the stretching direction, but at the same time do not enter the coupling regime as a consequence of the transverse strain. A straightforward solution to this is the application of linear arrays. Based on the assembly in wrinkled structures (see Section 4.2), Steiner et al. have applied particle lines to conduct mechanoplasmonic tuning (see Figure 9c).^[26] The applied spherical gold particles feature pronounced coupling along the lines with an absorbance maximum at around 760 nm as shown in Figure 9d. A dipolar mode is visible at 550 nm as the perpendicular spacing is sufficiently large (>5 radii)^[106] to exclude perpendicular coupling (even in the stretched state). Stretching of the flat PDMS substrate results in an increase of the interparticle distance (along strain direction) which evokes as an optical blueshift of almost 50 nm. Interestingly, the lines do not elongate homogeneously but fragment into plasmonic oligomers as displayed in Figure 9e. This is of special interest for energy transport (waveguiding)^[107-109] and sensing applications as these plasmonic oligomers are highly responsive to variations in the refractive index surrounding.^[110] Further relevance of such structures is found in the field of chiral plasmonics.^[111] As shown by the group of Kotov, lines of plasmonic colloids can be used for modulation of chiroptical activity via mechanical deformation.[112,113] These structures

are of potential interest for tunable nonlinear optics^[8] and optoelectronics.^[114]

4.2. Tuning of Lattice Coupling

The sensitivity and accuracy of optical responses toward mechanical deformation (and other triggers) can be modified favorably by a careful arrangement of the plasmonic particles. The aforementioned approaches share the following characteristics: On the one hand, the response behaves nonlinear, with high sensitivity at low strain and decreasing feedback at higher strains. On the other hand, the plasmonic resonance (especially in the coupled state) is comparably broad (mediocre quality factor). A sharper peak with a high quality factor would greatly improve the readout and detectability of minor changes. Both conditions can be overcome by utilizing SLRs instead of LSPRs for creating an optical feedback. The combination of elastomeric substrates and lattice resonances has been foremost studied by the group of Odom,^[37,38,115] who investigated the behavior of different lattice geometries prepared. Aside from this lithography-based work, colloidal self-assembly enables the preparation of plasmonic lattices on elastomers like PDMS. Appealing methods for achieving such mechanotunable plasmonic structures are interface-mediated and capillary-assisted assembly.

Recently, Gupta et al. have demonstrated a mechanotunable plasmonic lattice from colloidal self-assembly. The square







Figure 10. Mechanotunable colloidal lattice. a) Left: Stretching device with a colloidal plasmonic lattice on PDMS for combined microscopy/spectroscopy. Right: schematic of uniaxial stretching of a square lattice supported by an elastomer with a Poisson ratio of 0.5. b) Vis spectroscopy and respective FDTD simulations of a plasmonic square lattice with 440 nm spacing under strain (0–40%). Adapted with permission.^[15] Copyright 2019, American Chemical Society.

lattice was prepared via capillary-assisted assembly on PDMS that was nanostructured via LIL. The deformable lattice is shown in Figure 10a where it is mounted to a stretching device enabling mechanical deformation combined with in situ microscopy. The SLR peak of the square lattice with 440 nm periodicity is observed at 660 nm (see Figure 10b, black graph) which could be reproduced by FDTD simulations. Applying uniaxial strain to the lattice embedded in PDMS (Poisson ratio of ≈ 0.5) leads to the aforementioned increased spacing along the stretching direction (a' > a) and a perpendicular compression (b' < a). As a result, there is a pronounced splitting of the SLR, here expressed by a peak separation of up to 100 nm. Since the SLR is propagating perpendicular to the electric field, the blueshifted maximum corresponds to parallel polarization (along a'), while the orthogonal polarization (along b') is accompanied by the redshifted peak.

The linear response of the plasmonic lattice toward mechanical deformation renders such mechanotunable colloidal assemblies suitable for dynamic color tuning which is of interest for tunable filters and display technology.^[116,117] The narrow linewidth of the SLR results in strong and brilliant colors.^[39] Furthermore, they can be utilized for sensing since the signal provides good detectability and a pronounced response toward small strain changes. For these purposes, plasmonic lattices supported by thin elastomer films can be applied, as described in the work of Shen et al. The investigated isotropic deformation evokes linear shifts of a single SLR peak which enables tailoring of such narrow bandwidth resonances and is now accessible via colloidal methods.^[118]

5. Conclusion

In conclusion, we have shown that colloidal assembly strategies are well suited for the preparation of periodic plasmonic particle arrays that can support surface lattice resonances as the consequence of plasmonic/diffractive coupling. The progress in the field is driven by advances in modern particle synthesis: Core/shell particles with plasmonic cores and soft polymeric shells are ideal colloidal building blocks for various assembly

strategies where the shell can be used as a dielectric spacer and thus defines the lattice periodicity. Furthermore, the role of the polymeric shell can go beyond structural control by the integration of polymers with responsiveness toward environmental parameters such as solvent, pH, light, or temperature or complementary functionality such as by the integration of fluorescent or conductive polymers. These core/shell particles can be assembled into low-defect 2D lattices on fluid interfaces and subsequently transferred onto solid supports. Alternatively, the use of patterned substrates offers possibilities to direct colloidal assembly and thus further increase the pattern complexity. Here, we have especially emphasized approaches that are scalable, such as controlled wrinkling or interference lithography. Finally, multiple transfer or printing steps allow for the assembly of complex multilayered architectures. While classical lithography-based approaches for the fabrication of such plasmonic arrays are limited in terms of the total array dimensions, colloid-based fabrication schemes can overcome these limitations. At the same time, colloidal assembly is more energy-efficient and environmentally benign, as it is typically relying on synthesis in aqueous media and assembly rather than etching steps or processing using organic solvents.

An interesting aspect of colloidal assembly methods is the intrinsic compatibility with stretchable or even mechanotunable devices. Particle assemblies can be readily transferred onto stretchable substrates such as elastomers and the modular/ particle-based architecture is ideal for reversible mechanical deformation. Deformability is especially interesting for controlling chiroptical structures and surface lattice resonances, as the periodicities and symmetries in the arrays can be altered by the deformation. We discuss the perspectives of this mechanotunability for strain sensing and dynamic tuning of the resonance wavelength.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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