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

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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.

1. Introduction

Self-assembly of plasmonic colloids enables the fabrication of functional materials with optical responses that can capitalize on plasmon resonance coupling phenomena. 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. In contrast, periodic arrays of plasmonic nanoparticles with wavelength scale periodicities are able to support surface lattice resonances (SLRs). SLRs are collective, coupled modes between the localized surface plasmon resonance (LSPR) of the single nanoparticles and the diffractive modes of the lattice. 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. 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. The narrow linewidth of SLRs, implying long lifetimes, and their precise tunability by the lattice period, plasmonic material, particle shape, and the effective refractive index of the surrounding environment is of high relevance to several nanooptical applications like sensing, energy-transfer processes, and lasing. In the last decade, works addressing SLRs in periodic plasmonic lattices mostly rely on samples that were prepared lithographically, for example, by electron and soft interference lithography. 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. 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. 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 times and thus superior plasmonic properties. Losses due to scattering at grain boundaries and lattice defects in amorphous/poorly crystalline plasmonic nanostructures can broaden the LSPR and reduce its intensity. 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. 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. 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. 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. Further, self-assembly generally allows for the combination of different plasmonic materials, for example, to produce binary plasmonic lattices of gold and silver nanoparticles. 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. 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. While the influence of size heterogeneity has been studied in periodic lattices of plasmonic dimers consisting of silver disks with different sizes, 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 has 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. 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.

2. Results and Discussion

2.1. 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. The core–shell particles were synthesized by seeded precipitation polymerization 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. and Honold et al. 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 $d_{Ag} = 101 \pm 10$ nm (a) and gold cores with an average diameter of $d_{Au} = 100 \pm 8$ 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.

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. This was previously also reported by us and theoretically supported through Mie theory calculations.

Both types of core–shell particles were used to prepare periodic, plasmonic lattices using colloidal self-assembly at air/water interfaces. The assembly process for the formation of the self-templated honeycomb (hc) and Moiré lattices starting from hexagonally ordered arrays was recently reported by

![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.](image-url)
us.\textsuperscript{[22,26]} A detailed description of the assembly procedure and the sample characterization can be found in the Supporting Information.

2.2. 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 \( \mu \)m (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 $\alpha$ 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 $\alpha$ 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.

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.

2.3. 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

![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$_{dp}$), the quadrupolar LSPR (LSPR$_{quad}$), and the SLR from coupling to the $<0,1>$ 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).](Image)
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 ($\text{RI}_{\text{glass}} = 1.52$), the collapsed PNIPAM hydrogel shell ($\text{RI}_{\text{shell}} = 1.49$) and air ($\text{RI}_{\text{air}} = 1.00$).\textsuperscript{[3a,30]} On average this results in a higher effective RI of the environment compared to that of water with $\text{RI}_{\text{water}} = 1.332$. Due to the inhomogeneous RI environment coupling to the $<0,1>$ Bragg mode is restricted.\textsuperscript{[3b,30]} 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 $10 \times 10 \mu m^2$ 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 $295 \pm 42$ nm in the hc lattice. This distance is small enough to enable near-field plasmon resonance coupling.\textsuperscript{[21]} 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.\textsuperscript{[3b,c,5a,c]} We achieved this by spin-coating of a PNIPAM layer on top of the assembled structure.\textsuperscript{[5a,b]} 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 $<0,1>$ 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.\textsuperscript{[6,13,31]} For our samples, the coupling strength is most probably restricted because of positional disorder and relatively small domain sizes.\textsuperscript{[32]} 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.\textsuperscript{[3b]} The quadrupolar mode occurs at too short wavelength to contribute to the diffractive coupling.

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 ($\text{RI} = 1.49$, 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 $Q = \text{FWHM}/\Delta \lambda = 10$) 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 ($d_{c-c} = 432–512$ 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 $d_{c-c}$ as a consequence of the red-shift of the diffractive modes. The theoretical (0,1) diffraction wavelengths shift from 554 nm for the sample with smallest $d_{c-c}$ to 656 nm for the largest spacing. In addition, the SLRs become less intense and the peak width increases as $d_{c-c}$ 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 multi-domain samples and scattering losses that dampen the diffractive modes.\textsuperscript{[8]} The Ag-PNIPAM hc arrays show a quadrupolar LSPR contribution at approximately 410 nm (Figure 4a). As $d_{c-c}$ 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 $d_{c-c}$,
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. 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 (0,1) 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.[32a]

2.4. 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 ($d_{c-c} = 485–490$ nm) and thus are expected to show (0,1) diffraction modes at very similar wavelengths.[14] 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 $\alpha$ 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 $\alpha$.

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.

2.5. 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 ($d_{c-c} = 483$–$488$ nm). The SLRs of the hexagonal and Moiré structures almost perfectly overlap with resonance positions of $\lambda_{SLR} = 651$ nm and $\lambda_{SLR} = 650$ nm, respectively. Only the SLR of the hc structure is significantly blue-shifted to $\lambda_{SLR} = 629$ nm. This blue-shift of the hc structure in comparison to hexagonal lattice symmetries was also demonstrated in lithographically prepared samples by Humphrey and Barnes[13] 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 $\alpha$ 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, $d_{c-c} = 481$–$484$ nm). The hexagonal sample exhibits an SLR of $\lambda_{SLR} = 654$ nm, the Moiré structure of $\lambda_{SLR} = 651$ nm and the hc structure a clearly blue-shifted SLR of $\lambda_{SLR} = 633$ nm. Lastly the binary array structure which only exists as a Moiré and hc lattice (Figure 6c, $d_{c-c} = 487$–$488$ nm) gives very similar results with SLRs at $\lambda_{SLR} = 643$ nm and $\lambda_{SLR} = 631$ 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.

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 cm²-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 cm² area of the samples presented in this study, the self-templated assemblies contain approximately $10 \times 10^{10}$ 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 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.

3. 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 Humphrey[13] and Guo[14] 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 Afienieva.[33]

4. Experimental Section

Materials: Gold(Ill) chloride trihydrate (Sigma-Aldrich, ≥99.9%), sodium citrate dihydrate (Sigma-Aldrich, ≥99%), butylenylamine hydrochloride (Sigma-Aldrich, 97%), sodium dodecyl sulfate (Merck), N-Isopropylacrylamide (NIPAM; Sigma-Aldrich, 97%), N,N'-methylenebisacrylamide (BIS; Sigma-Aldrich, 99%), potassium peroxydisulfate (Fluka, ≥99%), silver nitrate (99.999%, Sigma), acetic 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.[28] These core–shell particles possessed a total hydrodynamic diameter of 336 nm (20 ºC, 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.[21] Overgrowth using silver was performed as previously published by Volk et al.[34] 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.[21] 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.[21] In order to enable the formation of SLRs the self-assembled arrays were overcoated with linear PNIPAM (40 000 g mol⁻¹) synthesized following a protocol from Ebeling et al.[34] 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 × 10 µm² and 40 × 40 µm² 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 pathlength (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. [5a]) 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 54d, 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 μm 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 silver[35] and gold[36] to literature values in order to perform a broadband source simulation (λ = 290–910 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.[37] (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 54c, 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: λ₅₉₀ = 290–910 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.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

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

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