Mechanically Tunable Lattice-Plasmon Resonances by Templated Self-Assembled Superlattices for Multi-Wavelength Surface-Enhanced Raman Spectroscopy

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Lattice plasmons, i.e., diffractively coupled localized surface plasmon resonances, occur in long-range ordered plasmonic nanostructures such as 1D and 2D periodic lattices. Such far-field coupled resonances can be employed for ultrasensitive surface-enhanced Raman spectroscopy (SERS), provided they are spectrally matched to the excitation wavelength. The spectral positions of lattice plasmon modes critically depend on the lattice period and uniformity, owing to their pronounced sensitivity to structural disorder. We report the fabrication of superlattices by templated self-assembly of gold nanoparticles on a flexible support, with tunable lattice-plasmon resonances by means of macroscopic strain. We demonstrate that the highest SERS performance is achieved by matching the lattice plasmon mode to the excitation wavelength, by post-assembly fine-tuning of long-range structural parameters. Both asymmetric and symmetric lattice deformations can be used to adapt a single lattice structure to both red-shifted and blue-shifted excitation lines, as exemplified by lattice expansion and contraction, respectively. This proof-of-principle study represents a basis for alternative designs of adaptive functional nanostructures with mechanically tunable lattice resonances using strain as a macroscopic control parameter.

1. Introduction

Due to their remarkable ability to confine light to the nanoscale, plasmonic nanostructures are the preferred platform for ultrasensitive spectroscopy techniques, such as surface-enhanced Raman scattering (SERS) spectroscopy.^[1,2] High and efficient signal enhancement typically demands a close match between

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the plasmon resonance wavelength and the excitation source.^[3,4] Plasmon resonances can be engineered through nanostructure composition and morphology, as well as the refractive index of the environment.^[5,6] In the case of superlattices, for example in the form of periodically arranged clusters of gold nanoparticles, another control parameter comes into play,^[7] namely the lattice period. Lattice resonances result from diffractively coupled localized surface plasmons of a substructure within a periodic arrangement.^[8] The periodicity, the center-to-center distance between adjacent plasmonic meta-atoms, is the key parameter for constructive (radiative) far-field coupling.

In the case of resonant excitation, lattice plasmons can generate intense electromagnetic fields,^[9–11] as required for ultrasensitive SERS spectroscopy. We have recently shown that the resonance band of square-array 2D supercrystals, fabricated by template-assisted colloidal self-

assembly of gold nanoparticles (NPs), can be tuned throughout the visible and near-infrared (NIR) range, as a function of the lattice parameter.^[12] The highest SERS performance was achieved at best match with the laser excitation. Combining short- and long-range interactions in such arrays can result in higher field enhancements. Tuning both the lattice period and the size of the substructures requires iterative remodeling of

Dr. J. L. Garcia-Pomar INL – International Iberian Nanotechnology Laboratory Braga 4715-330, Portugal Dr. A. Mihi Instituto de Ciencia de Materiales de Barcelona (ICMAB-CSIC) Bellaterra 08193, Spain Prof. L. M. Liz-Marzán, Prof. A. Seifert IKERBASQUE – Basque Foundation for Science Bilbao 48009, Spain Prof. L. M. Liz-Marzán Department of Applied Chemistry University of the Basque Country (EHU-UPV) Donostia-San Sebastián 20018, Spain the template structure and its repeated fabrication by electronbeam lithography (EBL), which is time-consuming and costly. This issue makes mode matching a complex and tedious task that generally results in a trade-off between excitation efficiency and signal enhancement.

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A key issue during fabrication is the rigid template that predetermines the plasmonic structure through the assembly procedure. We propose a more practical solution that allows for the subsequent modification of the lattice structure by physical or chemical external stimuli. Ideally, continuous and reversible tuning of the lattice periodicity would allow for a precise adjustment of the lattice resonance to the excitation wavelength of the laser, thus enabling a versatile screening of the most efficient SERS performance. Such a tunability could be achieved by changing the nanoscale spacing between gold nanoparticles within the substructures. In colloidal dispersions, dynamic tuning of plasmonic properties by distance control has already been demonstrated, for example through hydrophobic interactions,^[13] pH,^[14] or temperature variation.^[15] In most cases, such control mechanisms cannot work on solid (rigid) substrates or under dry conditions. Alternatively, the substrate on which the nanostructure is supported would provide access to further tunability by using elastomeric materials^[16] or through conformational changes of polymers under external stimuli.^[17,18] Several studies have been reported on the manipulation of plasmonic modes in substrate-supported nanostructures by tuning nearfield interactions between NPs.^[19,20] For instance, Baumberg and co-workers used dark-field spectroscopy to demonstrate the controlled detuning of a single plasmonic dimer under mechanical strain.^[21] Mechanical tuning of lattice plasmons has been applied to both all-dielectric^[22] and plasmonic^[23,24] lattice structures on stretchable supports. Expectations are high and numerous applications would benefit from the ability to implement active mechanical tuning, opening new avenues toward structural coloration with full-spectrum response,^[25] mechano-chromic materials,^[26] nanolasing,^[23] programmable plasmon-mode engineering,^[27] and broadband metasurfaces^[28] as multi-wavelength SERS substrates. Most of these approaches use top-down fabrication methods such as EBL, which offers excellent structural control on small areas. However, the current limits in scalability and resolution drive the search for bottom-up alternatives, such as nanostructuring by colloidal self-assembly.^[29,30] Notwithstanding, nanostructures made of colloidal building blocks present additional challenges on flexible supports. In particular, the balance between adhesive and cohesive forces plays a major role during mechanical tuning of colloidal particle assemblies on elastomeric surfaces, as demonstrated by Steiner and coworkers.^[31] Both detachment of the nanostructures from the support (adhesive failure) and structural fragmentation (cohesive failure) must be avoided by control of the interfacial chemistry.

Plasmonic nanostructures on elastomeric substrates show promising opportunities for next-generation sensing devices, realized by the combination of plasmonic tunability and mechanical flexibility.^[32] This also holds true for bendable devices and sensing on non-planar material surfaces such as food,^[33] plastics,^[34] or textiles. However, purposefully oriented macroscopic mechanical strain as a fine-tuning tool for nanostructural parameters still poses a challenge for the precise control of plasmonic modes. We expect highest SERS performance under resonant excitation conditions, where the symmetry of the lattice deformation plays a critical role for constructive diffractive coupling. Thus, mode-matching by postassembly adjustment of long-range structural parameters is expected to offer a relevant addition to near-field enhancements in plasmonic superlattices.

In particular, we present continuous and reversible tuning of lattice plasmon resonances by mechanical deformation of templated self-assembled gold NP superlattices on flexible substrates. As a proof of principle, we demonstrate the reversible mechanical tuning of a superlattice, made from a single template, for operation at two excitation wavelengths, using postassembly lattice deformations. The effects of symmetric and asymmetric lattice deformations on the optical properties were studied under both unpolarized and linearly polarized light. The SERS performance was confirmed to peak at resonant conditions, when the laser excitation coincides with the selected lattice modes. Mechanical strain thus serves as a macroscopic control parameter for the fine-tuning of lattice resonances and their efficiency for multi-wavelength SERS.

2. Results and Discussion

2.1. Self-Assembly of Gold Nanoparticles into Superlattices

For the preparation of highly regular supercrystal arrays, we performed template-assisted colloidal self-assembly of spherical gold nanoparticles. This method has been previously reported for a variety of ordered structures, such as micron-sized square pyramids and hexagonally close-packed NP clusters.^[10,11] Such superlattices have also been demonstrated to yield high SERS enhancement,^[35] with applications, e.g., for biosensing in complex media.^[36] For the assembly, a drop of a colloidal dispersion of monodisperse gold nanospheres, stabilized with polyethylene glycol (PEG), is left to dry under confinement by a template mold made of polydimethylsiloxane (PDMS), as shown in Figure 1a. For experimental details, see Section S1 in the Supporting Information. Because in this study both the template and the target substrate were made of PDMS, it was necessary to apply a thin layer of polyethyleneimine (PEI) to promote particle transfer and adhesion onto the target substrate. By using PEI as adhesion promoter,^[31] common problems regarding incomplete transfer could be efficiently avoided.

We worked with pre-patterned templates containing circular holes of 270 nm diameter and 87 nm depth, in a square grid with a period of 500 nm (Figure 1b). The resulting plasmonic superlattices consist of clusters, also called densely packed supercrystal substructures, within a regularly ordered arrangement that allows for intense far-field coupling.^[8] The 500 nm periodicity was specifically chosen because it is an ideal structure for the proposed proof-of-concept in plasmonic tunability, where the corresponding lattice resonance is centered around 700 nm, hence between the two targeted excitation wavelengths of 633 and 785 nm, as shown in Figure 1c.

We prepared superlattices using gold nanospheres of different sizes, ranging from 40 to 105 nm in diameter; all of them assembled with the same lattice period of 500 nm (see





Figure 1. Colloidal fabrication of superlattices on flexible supports: a) Templated self-assembly of plasmonic superlattices onto a PEI-coated PDMS substrate, which can be stretched by application of macroscopic strain. b) Schematic representation of the superlattice design with indicated lattice periods in horizontal $L_{\rm x}$ and vertical direction $L_{\rm y}$, as indicated. c) Experimental extinction spectra of transmitted light in the relaxed state. Photographs of the superlattice under white-light illumination in the d) relaxed and e) bent states. The green iridescent color results from light diffraction.

Figure S1, Supporting Information). Nanospheres of 40 nm diameter were found to yield the most suitable clusters, with high packing density and uniform cluster size. As an example, Figure 1d shows a photograph of a superlattice under white light illumination. At specific angles, an intense iridescent color can be observed due to light diffraction. Limited only by the size of the template, macroscale periodic arrangements of gold NPs were obtained over areas as large as one square centimeter. Due to the elastic nature of the PDMS substrate, it can be readily stretched or bent by mechanical deformation (see Figure 1e).

2.2. Superlattice Expansion and Compression

PDMS is a rubber-like elastic material with a Poisson's ratio near 0.5,^[37] which is why it contracts in the directions transversal to the direction of strain. This feature can be used to expand and compress superlattices post-assembly. By stretching the PDMS-supported superlattice, a gradual color change can be observed by the naked eye (Figure 2a), which indicates a change of the period and thus of the diffracted wavelengths. Nonetheless, this visual indication gives no information about the state of the cluster substructures nor about the precise change of the lattice period. Indeed, different scenarios could take place under applied stress, such as detachment and slipping of the clusters on the substrate; changes in the interparticle gaps; or fragmentation^[31] of the clusters into smaller units. Especially the latter two would induce dramatical changes in the resulting optical properties.^[38] The balance between cohesive (particleto-particle) and adhesive (particle-to-substrate) forces plays a critical role. If the cohesion between PEG-coated NPs is much larger than their adhesion to PEI-coated PDMS, the clusters can be expected to detach during stretching. In the reverse case, the applied stress could break up the clusters, as was recently evidenced by mechanical simulations using the lattice spring model.^[31] Both extreme cases must thus be avoided. Any structural changes to the cluster, including the number of NPs^[39] and interparticle distances,^[40] could have detrimental effects



700

600

500

30

(±1,±1)

600

500

Period (nm)

400

Figure 2. Tuning of lattice period: a) Digital photographs of a superlattice on PDMS under unidirectional stretching and white-light illumination, showing light diffraction by the grating structure. A gradual color change is observed upon stretching. b,c) Schematic drawings and e-SEM images of a 500 nm superlattice b) in the pristine state and c) elongated by 30%. d) Changes in the horizontal (black squares) and vertical periods (gray circles) under unidirectional strain, evaluated from e-SEM images. Dashed lines are guides to the eye. e) Calculated spectral position of diffraction anomalies (gray) at normal incidence, as a function of lattice period, predicted by lattice theory (Equation 1).

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20

Measured page 400

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5 mm

attice cont

10

Elongation (%)

on lattice plasmons and SERS enhancement. Electromagnetic simulations confirm that even small changes in gap sizes within clusters would have a significant impact on the optical properties and near-field enhancement (Figure S8, Supporting Information).

To study the structural changes of the superlattice upon mechanical deformation, environmental scanning electron microscopy (e-SEM) images were analyzed. In Figure 2b,c we compare the superlattice in the pristine/relaxed state and at 30% elongation. Please note, the observed dark vertical lines are artifacts due to charging during scanning (see also Figure S2, Supporting Information). The lateral resolution of e-SEM imaging does not allow a direct quantification of interparticle distances within individual clusters (see Section S3, Supporting Information). Nevertheless, statistical evaluation of the data obtained from image analysis yields reliable data for the relative change in interparticle distance when strain is applied. Figure S4d (Supporting Information) demonstrates that the interparticle gaps do not increase upon mechanical deformation of the substrate. Neither fragmentation, break-up, nor any other significant conformational changes could be observed, even after repeated stretching cycles. Therefore, we conclude that the clusters are robust against the applied mechanical stress and that the balance between cohesion and adhesion is appropriate for tuning the lattice period. In addition, we determined the lattice periods of the superlattice from e-SEM images taken at different uniaxial elongations (Figure S3, Supporting Information). At 30% elongation, the lattice periods in

stretching

ectional

the horizontal and vertical directions changed from 500 to 645 and 440 nm, respectively. Figure 2d shows that the magnitude of the horizontal expansion is almost twice the vertical contraction, as expected for an incompressible rubber-like material with a Poisson's ratio near 0.5, such as PDMS.

2.3. Asymmetric Optical Tuning by Unidirectional Strain

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Once we understood the conformational changes upon unidirectional strain, we focused our attention on the corresponding optical effects. Lattice plasmons rely on the constructive interference of scattered fields produced by the periodically arranged clusters.^[8,41] The lattice plasmon wavelength of a square array can be estimated from the wavelength of in-plane diffracted orders λ_{diff} , also known as Rayleigh cutoff wavelengths, describing specific lattice effects, in analogy to so-called Wood's and Rayleigh's anomalies^[42,43]

$$\lambda_{\text{diff}}(m,p) = \frac{\sqrt{n_{\text{sub}}^{2}(m^{2}+p^{2}) - n_{\text{top}}^{2} p^{2} \sin^{2}(\theta)} \pm m n_{\text{top}} \sin(\theta)}{m^{2} + p^{2}} \cdot L \quad (1)$$

The spectral position of this lattice resonance effect is determined by the period of the grating *L*, the refractive indices of interfacing media (substrate $n_{\rm sub} \approx 1.40-1.45$ for PDMS^[44] and superstrate $n_{\rm top} = 1$ for air), and the angle of incidence θ .^[45] The integers *m* and *p* correspond to the diffracted order. At normal incidence ($\theta = 0^{\circ}$) the degenerated diffraction modes of first order (±1,0) and (0,±1) are given by

$$\lambda_{\text{diff}}(\pm 1,0) = \lambda_{\text{diff}}(0,\pm 1) = n_{\text{sub}} \cdot L \tag{2}$$

Thus, a square lattice with a period of 500 nm on a PDMS substrate corresponds to a diffraction mode^[46] at 700 nm (asterisk in Figure 2e). To match the diffraction mode with the excitation lines at 633 and 785 nm, the grating period has to be reduced to ≈440 nm or extended to ≈550 nm, respectively. In fact, the diffraction mode could in principle be tuned even to an excitation line at 532 nm, corresponding to a lattice compression to \approx 380 nm. However, for efficient transfer of energy from the incident light into the lattice plasmon, this anomaly must also energetically overlap with the plasmon resonance of the substructure,^[8] i.e., the self-assembled clusters.^[47] Figure S5 (Supporting Information) shows the results of numerical calculations by the finite-difference time-domain (FDTD) method for the absorption cross section of an isolated cluster and the resulting broad resonance modes in the corresponding spectra (for details on modeling see Section S1, Supporting Information). Only in the case of mutual resonance, there is an additional gain in the local near-fields within the lattice,^[9,12] as required for SERS (Figure S6, Supporting Information). For that reason, the design of suitable lattice structures for efficient SERS excitation by mode matching is challenging, since several structural and optical parameters must be adjusted to each other at the same time.

One can assume that asymmetric lattice deformations would result in optical anisotropy, with the coexistence of two separate grating anomalies in orthogonal directions. Each anomaly should be located at a distinct wavelength, either blue-shifted for lattice compression or red-shifted for lattice expansion (cf. Figure 2e). Control over the optical properties is important because they represent the basis for the excitation of electromagnetic hotspots and SERS in plasmonic nanostructures.^[48,49] To better understand the influence of lattice variations on SERS measurements, first of all we need to correlate the optical properties with asymmetric deformations of the lattice. For this purpose, we performed UV/vis/NIR extinction spectroscopy in transmission geometry with a custom-made stretching device to study the changes in optical properties at a fixed sample position while applying unidirectional strain.

Figure 3 shows a UV/vis/NIR spectroscopic analysis under linearly polarized light, so that the influence on the optical



Figure 3. Optical changes for lattice expansion and compression during asymmetric unidirectional mechanical deformation: scheme of stretched superlattice and light polarization, along the direction of either a) expansion or b) compression. c,d) Experimental extinction spectra for various elongation states, according to the provided color scale. Comparison of experimental and simulated extinction spectra upon unidirectional strain and light polarized along the direction of e) expansion and f) contraction, in stacked representation. Black curves represent the optical properties of the superlattice in pristine conditions. Electric-field enhancement maps for the g) expansion and h) compression modes for an array with 15% of elongation, excited at the wavelength of the resonance peaks.



spectra of both lattice modifications could be studied separately. The basic theory of plasmonic lattices states that, for linearly polarized light and ideal orientation, the lattice plasmon excited along a principal direction should be plasmonically decoupled from the lattice plasmon in the perpendicular direction. However, depending on the structure of the subunits, near-field coupling effects can lead to transverse interactions. Polarization was adjusted along the direction of either expansion (Figure 3c,e) or compression (Figure 3d,f). For clarity, we used a simplified notation of expansion mode and compression mode below. The lattice plasmon of the superlattice in pristine/ relaxed state builds on a grating anomaly (first-order diffractive mode), giving rise to a sharp extinction band around 710 nm, together with a shoulder at 530 nm. This peak is assigned mainly to a mixture of the plasmon mode for individual nanoparticles^[50] and high-order longitudinal modes of the cluster, as shown in Figure S5 (Supporting Information).

Using light polarized along the axis of elongation, the lattice plasmon was found to red-shift from 710 to 805 nm, for a lattice elongation of 35% (expansion mode, Figure 3c,e). If the incident light is polarized along the axis of compression, a lattice plasmon blue-shift from 710 to 623 nm is observed instead (compression mode, Figure 3d,f). Hence, the polarization direction acts as a switch between both lattice plasmons. The evolution of the expansion and compression modes could also be reproduced by FDTD simulations, as shown in Figure 3e,f. Considering the multitude of parameters in this system (Section S1, Supporting Information) and irregularities of the self-assembled clusters, the agreement between experimental and theoretical data is remarkable. Minor discrepancies can be attributed to the presence of more than a single cluster configuration in real samples, which is likely to influence the coupling efficiency to the lattice plasmon. In addition, for the sake of simplicity, the interparticle spacing in the simulations was fixed to 1 nm. set by a shell of refractive index of 1.46 to emulate PEG. Nevertheless, the evolution of the lattice modes upon lattice deformation is consistent with the experimental results. Figure 3g illustrates that the expansion mode is supported by the entire cluster, while the compression mode presents a mode profile that enhances mainly the field in the lateral part of the cluster (Figure 3h). The spectral position of the diffraction modes matches well with the position of the cluster modes in isolated state (Figure S5). The lattice mode thus hybridizes with the different cluster modes to form lattice plasmons depending on their spectral overlap.

Considering that both modes are close to the usual excitation lines of 633 and 785 nm, this model system renders our structures suitable for use under both SERS laser line excitations. It should be noted that, next to the expansion mode, a broad peak can be observed between 650 and 700 nm, likely due to plasmon modes for the cluster substructures, not coupling to the lattice. In other words, the progressive tuning of the grating anomaly (diffractive mode) toward the red leads to decoupling of the clusters from the lattice. This observation is supported by FDTD simulations, which predict a similar contribution for an isolated cluster of nanoparticles (Figure S5, Supporting Information), with a broad band between 650 and 800 nm.

2.4. Symmetric Optical Tuning through Bidirectional Strain

We now have a clear understanding of the anisotropic optical response of asymmetrically deformed lattices. Since the plasmonic response strongly depends on the polarization state of the incoming light, the competition between transversal lattice plasmon modes may hinder the formation of efficient hotspots. Consequently, it would be advantageous to avoid symmetry breaking by applying a uniform strain in both directions. For this purpose, we used a custom-made 2D stretching device. Here, the sample was clamped at all four sides, so that strain can be applied symmetrically. Because this device can only apply positive strain, the experiments were limited to (symmetric) optical tuning of the *expansion mode*.

Figure 4 compares the mode evolution for asymmetric (Figure 4a,c) and symmetric lattice deformations (Figure 4b,d). By performing optical measurements with unpolarized light, we observed that the asymmetric deformation mainly leads to a blue-shift of the *compression mode* toward 633 nm. Though observable, the red-shifting *expansion mode* appears much weaker, which may be partly caused by the contribution of the cluster plasmon under non-resonant conditions to the lattice, as explained above. In addition, the imbalance between the



Figure 4. Optical effects of asymmetric (unidirectional) versus symmetric (bidirectional) lattice deformation: a,b) Schematic depiction of lattice deformations. Experimental extinction maps for a 500 nm superlattice under c) asymmetric and d) symmetric strain. Dashed lines indicate mode shifts. e) Corresponding experimental extinction spectra and f) comparison of the resonance shifts under asymmetric (blue squares) and symmetric deformations (red circles).

number of compressed and extended cluster gaps within the measurement spot favors the *compression mode*. Because of the finite size of the illuminated area, lattice expansion is accompanied by a decrease in the number of subunits with extended periods. On the contrary, lattice compression increases the number of subunits with shorter periods within the probed area. To further support our understanding of the mode evolution, the same experiments were also carried out with a superlattice of 600 nm period (Figures S9 and S10, Supporting Information). In this case, the pristine lattice plasmon was located at 840 nm, and the expansion mode shifted up to 930 nm at 30% elongation. The evolution of the modes observed during strain is fully consistent with our understanding, as detailed above.

Upon bidirectional symmetric stretching $(L_x = L_y)$, a completely different optical behavior was observed. Figure 4d shows a pronounced *expansion mode* that progressively redshifts (800 nm at 20% elongation). A second spectral feature develops around 600–650 nm, which could be attributed to lattice plasmons formed by the (±1, ±1) diffractive mode (Figure 2e). The red-shift and the secondary feature are corroborated by FDTD simulations as shown in Figure S7 (Supporting Information). Upon bidirectional strain, the intensity of the *expansion mode* is much higher than that under unidirectional strain. This effect is in agreement with the understanding of the lattice plasmon, because coupling can take place more efficiently in a symmetric lattice, where both lattice parameters can diffract the excitation light efficiently.

We thus conclude that, bidirectional symmetric stretching is the method of choice to obtain an intense expansion mode, as exemplified here for square superlattices. We found that most of the experiments reported in the literature used unidirectional strain and thus considered asymmetric mechanical deformations.^[24,27] Performing stretching experiments with bidirectional strain control allows us to avoid contraction of the sample and better controlled strain fields. Independent control over the periods in both axes allows for geometries that are not feasible with simple unidirectional stretching. To investigate the effect of symmetry on the optical properties of superlattices in more detail, we used a custom-made stretching device with separate control over both stretching axes. This allowed us to perform two-step stretching experiments: first, a square lattice was expanded into a rectangular lattice with a fixed vertical axis; the vertical axis was then gradually elongated to obtain a stretched square lattice. By stretching a square lattice into a rectangular one, we observed a redshift of the lattice plasmon, as expected. However, we also observed a significant broadening of the lattice mode (Figure S11, Supporting Information). By stretching from a rectangular lattice into a stretched square lattice, an additional red-shift of the expansion mode could be observed, but this time, the band became significantly sharper. A higher symmetry in superlattices leads to more intense and sharper lattice plasmon resonances, especially in the case of non-ideally aligned exciting fields or depolarized light, which is appealing for applications relying on high Q-factors, such as nanolasing.^[23] It is worth mentioning that a refractive-index matching layer^[51,52] on top of the plasmonic superlattices further decreases the spectral line width (Figure S12, Supporting Information), which is however not an option regarding SERS applications.

On closer inspection, it is noticeable that the starting spectra (0%, black curves, Figure 4e) for unidirectional and bidirectional stretching are not completely identical. The spectra differ by about 15 nm in their peak positions and the mode shapes are slightly different, which is due to the use of two different stretching devices. Whereas for unidirectional (asym.) stretching the sample was fixed on only two sides, for bidirectional (sym.) stretching all four sides had to be clamped to allow 2D deformations. Although all other measurement parameters were kept constant, owing to the two different clamping methods, slight differences in the 1D/2D pre-strain could not be entirely avoided. In combination with the high sensitivity of the optical properties to strain-induced deformations of the superstructure, minor variations in peak position and shape modulation of the lattice plasmon band are to be expected. Figure 4f compares the evolution of the lattice plasmons for asymmetric (blue squares) and symmetric deformations (red circles). For both methods of deformation, the expansion modes follow a linear trend for increasing elongation of the substrate. This behavior could be expected considering the linear relationship of the spectral position of the Rayleigh cutoff wavelength with the lattice period (cf. Equation 2, Figure 2e). The fact that both deformation methods yield almost identical plasmonic wavelengths, further supports the proposed concept of mechano-plasmonic tuning. This type of mode tuning is found to be fully reversible and could be validated by repeatedly switching between different elongation states with several stretching/ release cycles (Figure S13, Supporting Information).

2.5. SERS Performance of Strain-Deformed Superlattices

We finally investigated the impact of lattice tuning on SERS performance. Starting from the hypothesis that the best SERS performance relies on mode matching to the excitation laser,^[12] resonance states can be expected for asymmetric elongation of 30-40% for 633 nm excitation, and symmetric elongation of 10-20% for 785 nm excitation. To probe SERS enhancement, we used a low-molecular-weight model analyte, 4-nitrothiophenol (NTP), with a high affinity to adsorb onto gold and hydrophobic surfaces. Thus, the hydrophobicity of the PDMS support could be assumed to compete for the molecular adsorption of NTP. However, since the PDMS substrate was modified with PEI, its surface was rendered hydrophilic. For this reason, gold affinity should be the dominant factor here, driving the adsorption of the analyte into the hotspots between PEG-coated NPs. For more challenging analytes, i.e., with lower adsorption affinity, the surface chemistry of the hotspots could be chemically adapted to the requirements of the analyte of interest. To avoid detrimental effects on the PDMS substrate, such as reduced elasticity, no additional cleaning steps were applied. It is well known that oxidized PDMS exhibits a brittle interface, which would undergo irreversible cracking when stretched. Labeling with NTP was carried out by dropcasting a freshly prepared 1×10^{-6} M analyte solution, followed by washing with ethanol (Section S1, Supporting Information). NTP is a widely used performance marker in SERS spectroscopy, due to its intense stretching vibration of the NO₂ group at 1330 cm⁻¹.

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Figure 5. Mechanical tuning of SERS performance as a function of modematching: Schematic drawings of a) asymmetrically or b) symmetrically deformed superlattices. Stacked SERS spectra of an NTP-labeled superlattice under c) unidirectional stretching at 633 nm excitation, and under d) bidirectional stretching at 785 nm excitation. e,f) Experimental SERS enhancement as a function of lattice elongation, obtained from the intensity of the NO₂ stretching vibration (gray highlighted area in (c,d)) and normalized to the intensity in unstretched state. Enhancement was found to peak at resonant conditions between lattice plasmons and excitation lines. Dashed lines serve as guide to the eye. Gray highlighted areas indicate a spectral matching of the lattice modes with the corresponding excitation lines (*cf.* Figure 2e). g,h) Gain in enhancement predicted by FDTD modeling.

Figure 5 provides a summary of SERS experiments performed with both 633 and 785 nm excitation lasers, so as to investigate the effects of mode-matching by tuning the lattice parameters. The experiments were performed without an additional linear polarizer, so that it can be expected that the excitation light is partially depolarized by the Raman microscope optics. In principle, substrate stretching is accompanied by a decrease in the number of SERS emitters in the finite excitation volume (Figure S14, Supporting Information) and thus a decrease in signal intensity could be expected. However, in the case of 633 nm excitation and unidirectional asymmetric stretching (Figure 5c), the Raman fingerprint remains almost constant up to an elongation of 30%. At 35%, when the lattice plasmon and the excitation laser are in resonance, the intensity increases significantly by 1.8 times by symmetric stretching and 3 times by asymmetric stretching (Figure 5e)-normalized to the intensity in unstretched state. Further stretching, however, causes a new loss of signal intensity, which confirms that SERS generated by the *compression mode* is highly sensitive to changes in lattice period of ± 25 nm (equivalent to $\pm 5\%$). This is corroborated by numerical calculations of the dipole enhancement $|E|^2/|E_0|^2$ by the local electric field $E_{\rm loc}$ in the twofold amplification process, i.e., the augmented excitation of a molecular dipole by an incident photon (λ_{exc}) and the stimulated emission of a scattered photon $(\lambda_{sca})^{[3,47]}$

$$EF = \frac{\left| E_{loc} \left(\lambda_{exc} \right) \right|^{2}}{\left| E_{0} \left(\lambda_{exc} \right) \right|^{2}} \times \frac{\left| E_{sca} \left(\lambda_{sca} \right) \right|^{2}}{\left| E_{0} \left(\lambda_{sca} \right) \right|^{2}}$$
(3)

This first-order approximation of the change in enhancement factors (EFs of 10^6 – 10^7 , Figure 5g, right axis) upon unidirectional strain is in excellent agreement with our experimental observations.

In the case of bidirectional symmetric stretching and 785 nm excitation (Figure 5d), a similar trend was also observed. After an initial damping up to 4% elongation, the signal intensity increased ca. two-fold, with a maximum at 8-9% elongation, followed by a gradual decrease (Figure 5f). This behavior resembles the response curve of a resonance phenomenon, as one might expect for an excitation matching effect, also theoretically corroborated by FDTD simulations (Figure 5h). To test the repeatability of this effect, measurement cycles between different stretching states were performed (Figure S17, Supporting Information). An excellent repeatability was found when switching between 0 and 8% elongation. Figure S18 (Supporting Information) compares the SERS performance at 785 nm of a superlattice, deformed by either asymmetric unidirectional strain or by symmetric bidirectional strain. Both types of stretching result in principle in the same expansion mode and in either case an additional gain in SERS performance can be observed upon resonant matching of the lattice plasmon with the excitation wavelength. However, the gain is more pronounced for symmetric deformations (Figure 5d), which further confirms our conclusion that the lattice plasmon generated via symmetric lattice tuning is more suitable for SERS applications due to its more uniform excitability.

To illustrate the importance of the lattice mode for increased SERS efficiency, a substrate without structural order was prepared for comparison. For this purpose, a drop of a colloidal dispersion of Au nanospheres was drop-casted on PEI-coated PDMS without the spatial confinement of the nanostructured template. The resulting nanostructures consist of random domains (Figure S15, Supporting Information), so that any influence from periodic order can be excluded. During stretching, the SERS signal was found to dramatically decrease using 785 nm excitation and stayed almost constant using



633 nm excitation (Figure S16, Supporting Information). We attribute this behavior to a combination of the poorly excitable nanostructures as well as a decrease in the number of Raman marker molecules in the excitation volume upon stretching (Figure S14, Supporting Information). For structured samples, the latter is compensated by the gain in enhancement upon excitation matching, which does not occur in the unorganized sample. Indeed, the optical properties of the disorganized sample (Figure S15b, Supporting Information) indicate a poorly defined plasmon band, which did not show any significant changes upon stretching. We conclude that the hierarchical organization of the cluster into a periodic superstructure is the key to the observed SERS amplification. In both deformation scenarios, the highest gain in SERS performance was found by matching the lattice plasmon mode to the excitation wavelength, through fine-tuning of the lattice plasmon by postassembly adjustment of long-range structural parameters.

Apart from the direct application of superlattices on flexible supports, the presented technology can be used for screening of structural parameters and identifying the most-suitable SERS conditions, i.e., a contracted lattice of 450 nm for 633 nm excitation and an expanded lattice of 530 nm for 785 nm excitation. Unlike most SERS substrates that can only operate efficiently for a single excitation wavelength, mechanically tunable superlattices provide a broader usable excitation band. Within the spectral limits of the substructures' intrinsic plasmon bandwidth,^[28] mechanical tuning grants access to multi-wavelength SERS substrates.

3. Conclusion

We demonstrated mechanical tuning of lattice plasmon resonances using a model system of self-assembled nanoparticle superlattices on a flexible substrate. This model system allows for a modulation of lattice periods using strain as a macroscopic control parameter. In this way, the structural parameters of the superstructures could be reversibly readjusted while keeping the plasmonic substructures intact. We assume that deformation of the lattice has a major effect on the inter-cluster distances as inferred from the optical spectra. Intra-cluster distances might be affected as well, but we propose, to a much lesser extent for the elongation rates considered. We support this hypothesis by the fact that elongated superlattices showed intense SERS signals emanating from the cluster substructures, indicating that such hotspots are still active upon deformation. We investigated the optical changes caused by expansion and contraction of the lattice, as a means for active mechanical tuning of plasmonic properties such as the control over the spectral position of the lattice plasmon. Here, we revealed the inherent differences between asymmetric and symmetric lattice deformations by a correlation of optical and structural parameters, which was faithfully reproduced by electromagnetic simulations. Rectangular lattice geometries were found to exhibit a competition between compression and expansion modes. As a proof of concept, we demonstrated that both lattice expansions and contractions can be used to adapt a single lattice structure to either red-shifted or blue-shifted excitation lines, respectively. An additional gain in SERS performance was observed when the lattice was tuned in resonance with the excitation, as initially hypothesized. Moreover, the gain in SERS performance relies on the resonant matching of the intrinsic plasmon band of the substructure (individual NP clusters) and the extrinsic diffraction mode of the superstructure (periodic arrangement), which constitutes the lattice plasmon. Consequently, the tuning range for efficient multi-wavelength SERS is predominantly limited by the spectral bandwidth of the substructure. The proposed technology serves for fast screening for most-suitable superlattice designs and for guiding the development of other adaptive functional nanostructures with mechanically tunable optical properties.

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.

Keywords

lattice plasmons, plasmonics, SERS, surface-enhanced Raman scattering spectroscopy, template-assisted self-assembly

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