Surface Lattice Plasmon Resonances by Direct In Situ Substrate Growth of Gold Nanoparticles in Ordered Arrays

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1. Introduction

For plasmonic nanoparticles, the resonant condition of collectively oscillating conduction electrons occurs at specific frequencies of light depending on the nanoparticle size, shape, material, and local dielectric environment. This localized surface plasmon resonance (LSPR) effect can confine light in subwavelength volumes, resulting in the generation of an enhanced electric field. However, these resonances are typically short lived, due to intrinsic high radiative optical losses that limit the associated quality factors (<10). Nonetheless, arranging plasmonic nanoparticles into ordered arrays emerged as a convenient strategy to overcome this limitation and to boost the quality factors of the system. In this configuration the optical losses associated with LSPRs can be compensated under Bragg conditions by hybridization with the scattered waves in the plane of the array close to the position of the Rayleigh–Wood anomalies. This compensation generates lattice plasmon resonances, and offers an additional possibility for tuning the optical properties, depending on the angle of illumination and the geometrical parameters of the array. Due to their narrow bandwidth (<2 nm) and long lifetimes, lattice plasmon resonances already impact the enhancement and manipulation of light–matter interactions, sensing, displays, information storage, and anti-reflective materials. The development of a simple, scalable, and rapid technique that combines the benefits of top-down and bottom-up methods...
would improve access to finely tuned plasmonic ordered arrays tailored to desired applications. As of now, top-down methods benefit from their control over the positions of the particles and the generalizability of the substrates, where bottom-up approaches offer control over the surface chemistry and particle size and shape. Capillary-assisted, electrophoretic, and templated self-assembly can be used to generate nanoparticle arrays from colloidal building blocks, offering affordable alternatives to top-down electron beam lithography, focused ion beam lithography, and electro- and thermal deposition. Despite these advantages, beginning from colloidal suspensions often involves multistep, time-consuming processes that limit scalability. For instance, liters-scale batch synthesis requires precise temperature and additional rate control and ligand exchange requires the addition of large excesses of capping ligands and multiple centrifugation steps. Furthermore, the requirement of clean-room facilities, costly specialized equipment, and complex self-assembly steps present barriers preventing accessibility of plasmonic substrates.

In situ growth is an unconventional approach where plasmonic structures are formed starting from inorganic precursors directly on the target substrate material without any initial colloidal synthesis steps. The particles nucleate on the substrate, therefore, this process does not involve any batch synthesis, self-assembly, or ligand exchange, and time-consuming procedures can be circumvented. So far, the possibility to direct growth into tunable nanometric patterns has proven difficult to achieve via in situ growth. Recent strategies for site-directed in situ gold nanoparticle growth include crack-templated reduction lithography and similar methods. Despite the possibility of creating single-nanoparticle-wide features using these techniques, the patterns accessible are limited to lines with resolutions of microns to hundreds of nanometers. Chemical patterning via microcontact printing has been combined with in situ growth to grow gold nanoparticles selectively on tunable micron-scale features, but with limited control over the nanoparticle morphology. Similar results were observed with in situ growth on top-down lithographically patterned chemical layers. Block-copolymer micelle lithography represents a leading technique applying in situ growth, where addressable structures comprised of shape- and size-controlled plasmonic units are uniformly and reproducibly created with single-particle resolution. However, standard block-copolymer micelle lithography is generally limited to array periodicities up to ~300 nm, preventing access to lattice plasmon resonances in the visible and infrared. Moreover, due to the reliance of the patterning on the assembly of block copolymer micelles, the arrays are typically constrained to hexagonal lattices and the casting process can take up to a few weeks (unless combined with additional top-down or soft-lithographic steps). Current limitations of in situ growth methods include: i) controlling the particle morphology/uniformity, ii) fabricating easily modifiable patterns (and with good selectivity), and iii) producing arrays with sufficient quality to sustain lattice plasmon resonances. Ultimately, these barriers have reduced the popularity of in situ growth methods for the fabrication of plasmonic substrates compared to top-down nanofabrication (such as electron beam lithography) and/or the implementation of colloidal nanoparticles. Furthermore, a comprehensive mechanistic understanding of gold nanoparticle formation on substrates requires further study, and relatively little work has addressed fundamental synthetic aspects of in situ growth, especially compared to the body of work that has been developed for colloidal synthesis.

Here, we establish and demonstrate a straightforward in situ growth approach targeting tunable plasmonic lattices following a rapid bottom-up growth of gold nanoparticles onto chemically patterned reactive areas created by soft lithography. To fabricate these structures, water-soluble hydroxypropyl cellulose (HPC) sacrificial hole masks (or stencils), were applied to create patterned regions containing gold nanoparticle growth-active chemical ink. Subsequent site-selective growth of gold nanoparticles was performed with the addition of a droplet of growth solution onto the chemically patterned substrates in one rapid (<10 min), single synthetic step. We demonstrate that the composition of the growth solution can be modulated to alter the size and shape of the particles as they grow on the substrate. We apply a one-step direct surface growth to generate lattice plasmon resonances, showing that in situ growth techniques can be used for engineering plasmonic materials with low optical losses. The benefits of plasmonic nanoparticle patterning and direct engineering of lattice plasmon resonances by in situ growth can contribute to the development of more efficient quantitative chemical and biological sensors, plasmonic catalytic substrates and biomedical platforms, offering far-reaching impacts in a broad range of fields.

2. Results and Discussion

2.1. Chemical Nanopatterning with Thermal Nanoimprint Lithography

Gold nanoparticle arrays were fabricated on polydimethylsiloxane (PDMS) substrates following the creation of nanochemical patterns following a scalable and versatile soft lithographic method. Specifically, water-processable HPC stencils were prepared via thermal nanoimprint lithography (t-NIL) as shown in Figure 1A and applied to direct gold nanoparticle growth to specific areas containing a strong chemical reductant. Briefly, in the t-NIL process, aqueous solutions of HPC were spin-coated onto the substrate, then the film was placed in contact with a hard PDMS (hPDMS) mold. Pressure was applied to the mold (≈1 bar) as the substrate was heated above the HPC glass transition temperature (140 °C), generating patterned holes shaped by the mold (optimization of the applied pressure and substrate treatments are shown in Figure S2, Supporting Information). We demonstrate high-fidelity patterning of films ranging in height from tens to a few hundred nanometers (~30–330 nm), by comparing the measured and simulated differential refraction spectra for HPC thin films prepared with identical procedures on silicon (Figure 1B, and Figure S3 and experimental details, Supporting Information). After t-NIL, the imprinted photonic structures confer iridescence to the patterned films, as shown in Figure 1C and Figure S3, Supporting Information. Successful array transfer was confirmed via scanning electron microscopy (SEM) in films as low as ~30 nm (Figure 1D–F).
This result seems counterintuitive, because normally with t-NIL, uniform patterns are not attainable with HPC volumes that do not match the negative volume of the stamp, which in our case corresponds to a film height of >250 nm (Scheme S6, Table S1, and calculations, Supporting Information). Electron microscopy analysis shows that the PDMS substrate is imprinted following the t-NIL process (Figure 1G,H). Therefore, we hypothesize that the key to patterning films nearly an order of magnitude lower in height than the normally required minimum is the implementation of the deformable receiving substrate, which helps to push the HPC into the vacant features as shown in Figure 1I.\textsuperscript{[25–27,51]} This feature has important implications for the thickness of the residual layer. In standard t-NIL on rigid substrates, residual material remains in the imprinted features, usually measuring ca. 20 nm in height for the patterns used here.\textsuperscript{[49,50]} The removal of the excess material necessitates anisotropic reactive ion etching and cleanroom processing. Since we can pattern significantly thinner films, we estimate that the residual layer is accordingly greatly reduced (Figures S4 and S5, Supporting Information). Consequently, a quick (30 s) isotropic UV–ozone etch can effectively remove the excess HPC remaining in the holes. This etching step was successful for all HPC formulations that gave films with lower volume than the negative volume of the stamp (Figure S6, Supporting Information). Overall, the described procedure enables the reliable fabrication of HPC stencils with nanometric hole features (lattice parameter, $\Lambda = 600$ nm) without the use of any specialized or costly equipment or cleanroom fabrication. In addition, the same modified t-NIL technique can be extended from free-standing PDMS to glass-supported PDMS, improving...
In situ size- and shape-control. In standard colloidal systems for successful in situ growth into patterns and for fundamental understanding of colloids: i) the presence of impurities in the growth solution, ii) growth rate, and iii) excess ink leaching into the growth solution. Regarding impurities, the water source is known to contain strong reductants on the surface of the substrate, colloidal nanoparticles can still spontaneously form from the precursors in the growth solution.

The nucleation step normally incorporates a strong reductant such as sodium borohydride for the fast, uniform formation of seeds from the gold precursor. The following growth step instead includes weaker reductants, such as ascorbic acid, capable of reducing Au(III) to Au(I), but confining the final reduction to Au(0) to the seed surface, promoting controlled growth. The seed-mediated synthesis scheme ensures suppression of later secondary nucleation events from occurring in the growth solution that would negatively affect size distribution and shape yield.

One of the most important aspects explored here is the limitation and control of secondary nucleation, which has proven to be a particularly difficult challenge for in situ growth systems. Here, the strong reductant ink is applied only on the substrate to mimic the spatially selective nucleation and growth processes used in colloidal synthesis, while the mild reducing agent ascorbic acid is added to the growth medium to facilitate the first reduction step of the gold salt from Au(III) to Au(I). Although in our in situ growth scheme, we are only providing strong reductants on the surface of the substrate, colloidal nanoparticles can still spontaneously form from the precursors in the growth solution. Thus, secondary nucleation for in situ systems can be described as the uncontrolled formation of nuclei away from sites explicitly containing the strong reductant, which contributes to irreproducible consumption of reagents and solution-deposited particles outside the pattern.

Even though nucleation can be achieved with the sole use of the physisorbed ink, our motivation behind adding ascorbic acid is to reduce the growth time and use of lower concentrations of gold precursor. In fact, using only a surface-bound strong reductant usually requires ~5 times more gold salt and hours to days long incubation. Continu
play important roles in colloidal synthesis, especially for the synthesis of anisotropic particles.\cite{54,61} Recent work shows that faster growth kinetics can favor colloidal nucleation over nucleation on the substrate.\cite{54} Therefore, we modulated the rate of the reaction by changing the type and concentration of the surfactant (cetyltrimethylammonium chloride or bromide, CTAC or CTAB, respectively). Lastly, we tested different inking methods and ink concentrations. The appearance of LSPR peaks evaluated by ultraviolet-visible spectroscopy indicated the occurrence of secondary nucleation, and the maximum intensity of the peaks was monitored over 15 min to track the severity of unwanted nuclei formation under different growth conditions (Figure 2D,E, and Figure S8, Supporting Information). Overall, growth solutions containing high-performance liquid chromatography (HPLC) grade water, and 25–50 $\times 10^{-3}$ M CTAB gave the least secondary nucleation (Figure 2D). This optimized growth formulation was fixed and the application of chemical ink via different routes was tested. Aside from vapor deposition, the least amount of secondary nucleation was observed when dilute (1% or 0.1%) solutions of the ink were spin-coated onto the substrate (Figure 2E). Spin coating dependably produced patterns, and all conditions appeared to give similar nucleation site densities (Figures S4, S9, and S10, Supporting Information). Therefore, the 0.1% solution was selected for the following sections. After 10 min of growth, the products appeared to have a different crystal structure and twinning, and isotropic products, triangles, rods and other platelets could be observed (Figure 2F–I). In the next section, we explore size and shape modification of the products.

2.2. In Situ Size and Shape Modification

Although little prior work has addressed mechanistic aspects of substrate-grown particles,\cite{53–55,63–66} fundamentals of in situ growth remain vastly unexplored compared to colloidal batch systems.\cite{59} Limiting the growth-active areas to diameters of $<100$ nm has the potential to enable tighter control over both nucleation and growth conditions. Next, we demonstrate the capability to modulate the size and morphology of the synthesized particles by changing the growth medium constituents and parameters, following concepts derived from colloidal synthesis.

Figure 3. A–D) SEM images of patterned nanoparticle substrates after 1 min (A), 2 min (B), 5 min (C), and 10 min (D) growth with a growth solution containing cetyltrimethylammonium bromide (capping ligand/surfactant), gold salt, and ascorbic acid as a mild reducing agent. E–H) Size distributions for the 1 min (E), 2 min (F), 5 min (G), and 10 min (H) samples (150 nanoparticles each, $n = 10$). I,J) Representative SEM images showing pattern yield and common defects: multiple particles per area (pink circles), vacancies (purple circles), and particles outside the pattern (green areas). Patterned regions with single particles are indicated with a white circle ($n = 10$).

Figure 2A–D, see Materials and Methods, Supporting Information, section for details). After 1 min of growth, the average particle size reaches $40 \pm 14$ nm (Figure 3E), which is relatively fast compared to colloidal synthesis.\cite{24,67,68} At 2 min, the products nearly double in size to $70 \pm 30$ nm (Figure 3F). Growth times of 5 and 10 min result in nanoparticles with similar diameters ($120 \pm 40$ and $110 \pm 40$ nm, respectively, Figure 3G,H). This behavior is consistent with other in situ growth studies.\cite{28,58,69,70} Another interesting aspect to consider is the shape distributions of the nanoparticles grown. In colloidal synthesis of gold nanostructures, mixtures of various anisotropic (elongated structures, platelets) and isotropic (multi-twinned objects, cubes, pyramids) are obtained if no shape-control strategy is used during growth.\cite{71–73} We observe similar behavior in the case of in situ grown particles. Even though the limitations of environmental SEM prevent us from distinguishing between different isotropic products (Figure 2F), we were able to identify platelets (Figure 2G,I) and rod-shaped geometries (Figure 2H), enabling us to evaluate their percentages and/or shape yield. Along with a change in the average nanoparticle diameter, shorter growth times were associated with lower percentages of total platelet and rod-shaped products. We estimate that the percentage of isotropic products decreased from $\approx60\%$ at 10 min to $\approx90\%$ at 1 min ($n = 150$ nanoparticles, Figure S11 and Table S2, Supporting Information). After 5 min, the nanoparticles formed at the specified nucleation sites no longer increase in size, possibly due to the onset of secondary nucleation effects. This hypothesis is supported by our evaluation of the patterning yield presented in Table S3, Supporting Information, where the percentage of particles outside the pattern slightly increases from 10% to 14% between 5 and 10 min.
Regarding patterning evaluation, various kinds of defects in the arrays are observed (Figure S1). Standard defects include vacancies (purple circles), multiple particles per region (pink circles), and particles outside the patterned region (green arrows). The patterning yield was evaluated as the percentage of ink-containing regions that produced nanoparticles across all growth times as \(\approx 80\%\) (detailed evaluation summarized is in Figure S1 and Table S3, Supporting Information). The total percentage of nanoparticles located within the growth active regions was estimated to be \(\approx 90\%\), indicating a strong preference for nucleation and growth within the pattern features due to the chemical contrast created by the presence and absence of the ink.

The identification of the sources of defects could assist in the future development of our in situ growth method; therefore, we next elaborate on this topic. Nanoparticles outside of the pattern (\(\approx 10\%\) of all particles) result either from secondary homogeneous nucleation events in the growth solution (followed by particle deposition on the surface), non-specific spontaneous nucleation on regions without ink, or defects in the HPC mask. The appearance of vacancies in the electron microscopy images could be caused by resolution limitations of environmental SEM, which complicates imaging particles smaller than 2 nm. If instrument resolution was the primary cause of observed vacancies, one would expect these small nuclei to grow eventually into larger, more easily measurable nanoparticles. However, the percentage of vacancies remains constant when growth time is increased from 1 to 10 min; therefore, we infer that the vacancies do not contain nanoparticles. Another hypothesis to explain the vacancies can be related to defects in the HPC stencil, causing local removal of the ink during the washing step. The exploration of different chemical inks to increase the chemical contrast of the patterned regions and the substrate could be pursued in the future to reduce the abovementioned defects. Finally, both the presence of nanoparticles that are not centered in the patterned area and the growth of multiple particles in certain regions can arise from the size mismatch between the growing particles and the patterned features, with the latter being much larger (>270 nm). Nonetheless, the average number of nanoparticles per patterned area corresponds to 2 particles per circular region (not counting vacancies). This is an important observation because it suggests that once the initial nuclei are formed, their growth is favored over the later formation of new nuclei. The formation of new nuclei is disfavored due to the preference for continued growth on the already-formed nuclei and/or due to charge screening affecting the transport of gold salt to the substrate.\(^{61,73}\) Moreover, this statistic gives us an estimate of the number of particles on each substrate as \(\approx 2 \times 10^8\) particles/substrate, or \(\approx 2 \times 10^9\) particles mL\(^{-1}\) of growth solution (assuming 100% yield of the t-NIL and ink patterning). The seed concentration in colloidal synthesis is usually 2–4 orders of magnitude higher (typical values for colloidal synthesis range between \(10^9\) and \(10^{11}\) seeds mL\(^{-1}\) of growth solution), giving us a much higher H\(_2\)AuCl\(_4\) to nanoparticle ratio.\(^{61,68}\) This difference provides an explanation for the speed of growth and offers possible improvements to target smaller nanoparticles and/or slower kinetics.

Next, we demonstrate generating anisotropic shapes directly on the substrate through post-modification and overgrowth of the arrays prepared after 5 min of growth. Previously, in situ overgrowth has been performed on colloidal assemblies to create unique geometries, such as Janus nanostructures, core-shell, hybrid and anisotropic/branched structures,\(^{94,75}\) which enable control over the plasmonic near-field with applications for photothermal or sensing applications, for example.\(^{52,46,76,77}\) Here, we target overgrowth of branched nanostars, which are attractive due to high localization of electromagnetic fields present at their sharp tips,\(^{46,76,78}\) their high extinction in the near-infrared biological window, and their capability for thermoplasmonic heating.\(^{46,79}\) The nanoparticle arrays were overgrown by subsequent incubation in a nanostar growth solution containing additional gold precursor and shape-directing reagents (silver nitrate, laurylsulfobetaine, hydrochloric acid, and ascorbic acid, Figure 4A). Similar to the first growth step, synthetic conditions were optimized to minimize secondary nucleation away from the substrate within the 5 min overgrowth time by lowering the pH of the growth medium, which limits the reducing strength of ascorbic acid.\(^{46}\) Following the overgrowth step, the substrate exhibited a change in color from red to dark blue. The extinction spectra after 5 min of standard nanoparticle growth with the cetyltrimethylammonium bromide growth solution gives one dominant LSPR dip at 575 nm, and the samples following 5 min of nanostar overgrowth exhibit high extinction in the near infrared region at 985 nm, matching the expected plasmonic response Figure 4B.\(^{46}\) The corresponding colloidal recipe for the one used here generally results in three main products: spheres, and low and high aspect ratio nanostars.\(^{46,76}\) However, electron microscopy characterization interestingly showed a high yield of one major, highly branched product (Figure 4C,D). The yield of the nanostar arrays over a larger area (measuring ca. 2000 \(\mu\)m\(^2\)) can be appreciated in Figure 4E. Altogether, the data presented in Figure 4 indicate that although certain concepts might transfer from colloidal to substrate growth (e.g., applying shape-directing reagents to promote anisotropic growth), important differences remain between the two environments that can significantly affect the shapes of the final products. The in situ surface growth strategy reported here represents an ideal platform for the exploration of such effects.\(^{46}\)

2.3. Geometrical Tuning of the Array and Lattice Plasmon Resonance Characterization

Perhaps the most striking advantage of combining t-NIL and in situ growth resides in the preparation of ordered plasmonic arrays with arbitrary geometries, achieving control at the same time over both LSPRs and lattice plasmon resonances.\(^{45–50}\) Although past and recent work proposed this possibility in relation to other in situ growth schemes, lattice plasmon resonances have not previously been demonstrated experimentally using only direct surface growth.\(^{16–19}\) The spatial and geometrical constraints of the state-of-the-art methods prevent engineering lattice plasmon resonances (as well as more complex light–matter interactions),\(^{50,82}\) limiting the application of in situ growth for the design of metasurfaces and intricate plasmonic systems. Our in situ growth approach overcomes two major barriers, namely the requirement for lengthy self-assembly steps and the flexibility in array periodicity by modifying the hPDMS.
Here, we measure lattice plasmon resonances for arrays with lattice parameters ($\Lambda$) of 400 and 500 nm, in addition to the $\Lambda = 600$ nm samples shown in Figures 1 and 3 (Figure 5A–F and Figures S13–S15, Supporting Information). Patterned in situ growth was achieved in all cases.

With the intention of maximizing the generation of lattice resonances through far-field coupling between the plasmonic units of the array, the particles were covered with a thin layer of soft PDMS after growth was complete. This step ensures a uniform refractive index environment around the plasmonic lattices, facilitating the propagation of the scattered field within the lattice plane.[$^3$] Sharp lattice plasmon resonances were observed in the transmission profile under this refractive index matching condition (Figure 5G–J), sample preparation details are given in Scheme S5, Supporting Information) giving, to the best of our knowledge, the first demonstration of lattice plasmon resonances via a purely in situ synthetic route, all without batch synthesis, self-assembly, top-down fabrication, nor costly and specialized equipment. Overall, this result shows that in situ growth can offer an inexpensive, simple, and rapid alternative for accessing collective plasmonic responses.

As expected, the wavelengths of the lattice plasmon resonances depend on the lattice parameter used for the preparation of the HPC masks (Figure 5G). Specifically, the most intense lattice plasmon resonances are expected to emerge in proximity to the first-order diffraction line, the spectral position of which can be predicted using the following simplified equation:[7]

$$\lambda = \Lambda \sqrt{n \sin \theta}$$

(1)

where $\Lambda_{x,y}$ represents the lattice parameters in the two orthogonal in plane directions, $n$ is the refractive index of the surrounding medium, and $\theta$ is the illumination incidence angle. At normal incidence, where $\theta$ is defined as zero, for a square lattice where $x = y$, and with $n_{\text{PDMS}}$ estimated to be 1.4, the predicted wavelengths can be calculated as: 560 nm for $\Lambda = 400$ nm, 700 nm for $\Lambda = 500$ nm, and 840 nm for $\Lambda = 600$ nm. In the 400 nm lattice parameter samples, the predicted lattice plasmon resonance overlaps with the LSPR of the gold nanoparticles and can be identified as a shoulder at 560 nm in the transmission spectrum. For the 500 nm lattice, a dip is observed at 698 nm, close to the predicted lattice plasmon resonance position. In the 600 nm lattice sample, the lattice plasmon resonance is observed at 826 nm (Figure 5G). The discrepancies compared to the predicted positions are common and can be attributed to factors including the effects of the CTAB gold nanoparticle coating, and/or the differences in PDMS refractive index as a function of composition and curing conditions.[22]

The identification of the aforementioned dips as lattice resonances is confirmed by measuring their spectral variation with illumination incidence angle (Figure 5H–J).[22] The dashed lines in Figure 5H–J are analytical calculations of the angular dependence of the Rayleigh–Wood anomalies. Apart from refractive index and lattice parameter, this dependence will also be modulated by the azimuthal angle of the array relative to the illumination (see discussion in Materials and Methods, Supporting Information). Additionally, the quality of the $\Lambda = 600$ nm array is also confirmed by the appearance of a second-order diffraction line (Figure 5I). Overall, the experimental data matched the predicted behavior, confirming the presence of lattice resonances.

Additionally, the quality of the observed lattice plasmon resonances was evaluated by calculating the quality factor ($Q_E$):

$$Q_E = \frac{\omega}{\Delta(\omega)}$$

(2)

where $\omega$ is the spectral peak position, and $\Delta(\omega)$ is the full width at half maximum of the peak. Using this relationship, we evaluate $Q_E = 29$ for $\Lambda = 600$ nm and $Q_E = 21$ for $\Lambda = 500$ nm. For the $\Lambda = 400$ nm array, we are unable to estimate the $Q_E$ since the diffraction line is blue-shifted relative to the lattice resonance peak, producing an asymmetric Fano profile, as described in a prior publication[22] (details on $Q_E$ calculations are in the optical characterization section, Supporting Information).
The $Q_0$ for single-nanoparticle arrays prepared from colloidal suspensions typically fall within the range of $Q_0 = 10–30$.$^{[3,22,83]}$ Thus, the performance of our arrays are on par with state-of-the-art methods based on single-particle assembly, despite the patterning defects and deviations in nanoparticle morphology that we observe. These results may be unexpected considering that our patterning yield is $\approx 80\%$ (Figure 3I,J, and Figure S12 and Table S3, Supporting Information) and our shape-yield is $\approx 80–90\%$ (Figure S11 and Table S2, Supporting Information), and any array defects would lead to broadening of the lattice resonance.$^{[3,22,84]}$ However, recent simulations by Manjavacas and co-workers suggest that by reducing the dimensions of the repeating unit below 100 nm, it is possible to achieve narrow LPRs, and that this effect is even more dramatic for realistic repeating unit below 100 nm, it is possible to achieve narrow and co-workers suggest that by reducing the dimensions of the plasmonic materials engineering.

Thus, the performance of our arrays are on par with state-of-the-art methods based on single-particle assembly, despite the patterning defects and deviations in nanoparticle morphology that we observe. These results may be unexpected considering that our patterning yield is $\approx 80\%$ (Figure 3I,J, and Figure S12 and Table S3, Supporting Information) and our shape-yield is $\approx 80–90\%$ (Figure S11 and Table S2, Supporting Information), and any array defects would lead to broadening of the lattice resonance.$^{[3,22,84]}$ However, recent simulations by Manjavacas and co-workers suggest that by reducing the dimensions of the repeating unit below 100 nm, it is possible to achieve narrow LPRs, and that this effect is even more dramatic for realistic finite systems.$^{[84]}$ These observations lead us to hypothesize that the reduced dimensions of our in situ grown nanoparticles, and the absence of optical losses due to strong near-field coupling within the repeating unit (as for cluster plasmonic arrays), explain our observation of relatively sharp lattice resonances despite the presence of defects. Even though the fabricated arrays are less uniform than those prepared by state-of-the-art top-down$^{[3,85]}$ or colloidal synthesis/self-assembly approaches,$^{[22,23]}$ the demonstration of lattice plasmon resonances with bottom-up in situ substrate growth highlight its potential as a straightforward and easily accessible route for plasmonic materials engineering.

3. Conclusions and Prospects

A modified t-NIL protocol was used to pattern HPC thin films on soft polymeric substrates. This technique produced periodic structures with minimal residual layers such that water-processable sacrificial stencils can be created in a standard laboratory environment without special equipment. The sacrificial HPC masks were used for chemical patterning and subsequent site-selective bottom-up gold nanoparticle growth. The particle size and shape were controlled directly on the substrate by altering the growth time and growth media composition, respectively. The use of t-NIL provides improved flexibility for modifying the pattern increments over a wide range by changing the mask features without adjusting the patterning process or increasing the processing time. Following optimization of the chemical inking method and the nanoparticle growth solution, lattice plasmon resonances were demonstrated for arrays with periodicities of 400, 500 and 600 nm, giving tunable lattice plasmon resonances from the visible to the near infrared. The versatility in tuning the array geometry can be applied for potentially targeting lattice geometries giving collective responses beyond the near infrared, into the mid- or even far-infrared regions. The developed method overcomes limitations that have, until now, prevented the realization of lattice plasmon resonances using solely in situ growth, constituting significant progress for this class of approaches. Future work can target the fabrication of hybrid materials and superstructures with multiple synthetic steps, in order to engineer complex optical responses, like what has been achieved via metal nanoparticle–polymer systems.$^{[86,87]}$ The design and fabrication of sensors relying on surface-enhanced Raman spectroscopy can also be the target of future exploration.$^{[29,30,65]}$ especially since patterning can assist in controlling hot-spot density.$^{[88]}$

Regarding fundamental synthetic aspects, understanding the roles of substrate wettability, particle–substrate interaction, secondary nucleation, the balance of reducing agents on the
substrate and in solution, effects of surface charge, chemical environment, and screening effects can help to create more reliable protocols achieving gold nanoparticle arrays and pave the way for new synthetic possibilities in the future.\[92,93]\] Shape control for in situ-grown particles has only been briefly studied compared to colloidaly synthesized particles and the need to probe various aspects of the growth thoroughly remains. In this regard, the in situ growth method presented here is versatile for future investigations studying wet-chemical shape control and selective surface growth. Furthermore, because the nanoparticles are fixed on the substrate, colloidal stability no longer represents a barrier to be considered, providing greater opportunities for testing unconventional growth conditions (e.g., surfactantless synthesis) or facile tailoring of the nanoparticle ligands. We anticipate that nanoparticle–substrate interactions will represent important aspects to explore, which can potentially be tuned via the selected metal,\[92,93\] selected ink, or the chosen substrate. The chosen substrate represents even more opportunities, that is, replacement of PDMS with different soft polymers,\[94,95\] conductive polymers,\[96,97\] hydrogels\[98\] and 2D materials.\[99,100\] In addition, the physical or chemical properties of the substrate could potentially be used as templates to facilitate the rotational order of products.\[100,102\] Ultimately, the presented methodology can bring a new perspective for the development of innovative synthetic paradigms for the growth of plasmonic nanoparticles and can impact the fabrication of solid-state platforms that take full advantage of the catalytic, optical, and magnetic properties of plasmonic nanoparticles.

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

Acknowledgements
The authors thank Camilla Dore for her advice and contributed expertise on the fabrication of HPC films. The authors extend their gratitude to Jose Mendoza Carreño for his assistance with the optical characterization of the gold nanoparticle arrays. This project had received funding from the Spanish Ministry of Science and Innovation through grants FUNFUTURE (CEX2019-000917-S), (FUNFUTURE, in the framework of the Spanish Severo Ochoa Centre of Excellence program) and PID2019-106860GB-I00 (HIGHHN). L.S. and A.M. thank the Spanish National Research Council (CSIC) for funding via the I-LINK 2020 international travel grant, which facilitated international exchange period necessary for completion of this work. L.S. and Y.C. research is supported by the 2020 Post-doctoral Junior Leader-Incoming Fellowship by “la Caixa” Foundation (ID 100010434, fellowship code LCF/BQ/PI20/11760028). Y.C. acknowledges the auspices of the UAB material science doctoral program. G.A.V.W. thanks the UCLA graduate division for funding through the University of California Office of the President Dissertation Year Fellowship. S.J.J. acknowledges support from the National Institutes of Health (NIH) Common Fund through a NIH Director’s Early Independence Award co-funded by the National Institute of Dental and Craniofacial Research and Office of the Director, NIH Grant DP5OD028181. S.J.J. and G.A.V.W. acknowledge support through a Scholar Award from the Hyundai Hope on Wheels Foundation for Pediatric Cancer Research. P.S.W. thanks the National Science Foundation for support through Grant #CHE-2004238.

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
Experiments were designed by G.A.V.W. and L.S. Data were collected by G.A.V.W., L.S., and Y.C. G.A.V.W. and L.S. led the optimization of the HPC stencil fabrication. G.A.V.W., L.S., and Y.C. performed the synthesis optimization of the AuNPs into arrays. Morphological characterization of the AuNPs was performed by G.A.V.W. and L.S. Optical characterization was carried out by L.S. and Y.C. The manuscript was written by G.A.V.W., L.S., S.J.J., P.S.W., and A.M., with assistance from all other authors. All authors have given approval to the final version of the manuscript.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
bottom-up synthesis, in situ growth, lattice plasmon resonance, plasmonic arrays

Received: June 13, 2022
Revised: July 13, 2022
Published online: August 15, 2022
[78] E. Lenzi, D. Jimenez de Aberasturi, M. Henriksen-Lacey, P. Piñeiro, A. J. Muniz, J. Lahann, L. M. Liz-Marzán, ACS Appl. Mater. Interfaces 2022, 14, 20708.

[79] A. Casu, E. Cabrini, A. Donà, A. Falqui, Y. Diaz-Fernandez, C. Milanese, A. Taglietti, P. Pallavicini, Chem. – Eur. J. 2012, 18, 9381.

[80] J.-Y. Kim, J. Yeom, G. Zhao, H. Calcaterra, J. Munn, P. Zhang, N. Kotov, J. Am. Chem. Soc. 2019, 141, 11739.

[81] E. S. A. Goerlitzer, R. Mohammadi, S. Nechayev, K. Volk, M. Rey, P. Banzer, M. Karg, N. Vogel, Adv. Mater. 2020, 32, 2001330.

[82] P. T. Probst, M. Mayer, V. Gupta, A. M. Steiner, Z. Zhou, G. K. Auernhammer, T. A. F. König, A. Fery, Nat. Mater. 2021, 20, 1024.

[83] M. Juodėnas, T. Tamulevičius, J. Henzie, D. Ėrts, S. Tamulevičius, ACS Nano 2019, 13, 9038.

[84] A. Manjavacas, L. Zundel, S. Sanders, ACS Nano 2019, 13, 10682.

[85] Q. Le-Van, E. Zoethout, E.-J. Geluk, M. Ramezani, M. Berghuis, J. G. Rivas, Adv. Opt. Mater. 2019, 7, 1801451.

[86] K. Volk, T. Honold, D. Feller, M. Karg, Adv. Mater. Interfaces 2021, 8, 2100317.

[87] Y. Brasse, V. Gupta, H. C. T. Schollbach, M. Karg, A. Fery, Adv. Mater. Interfaces 2020, 7, 1901678.

[88] L. Osinkina, T. Lohmüller, F. Jäckel, J. Feldmann, J. Phys. Chem. C 2013, 117, 22198.

[89] A. G. Mark, J. G. Gibbs, T.-C. Lee, P. Fischer, Nat. Mater. 2013, 12, 802.

[90] G. Klöss, M. Miola, D. S. Sutherland, J. Phys. Chem. C 2019, 123, 7347.

[91] A. Design, M. Miola, A. Ravishankar, Nano Res. 2019, 12, 1635.

[92] B. Viswanath, P. Kundu, A. Halder, N. Ravishankar, J. Phys. Chem. C 2009, 113, 16866.

[93] M. Ishii, Z. Lyu, M. Zhao, R. Chen, Q. N. Nguyen, Y. Xia, Chem. Rev. 2021, 121, 649.

[94] E. S. Abdel-Halim, S. Al-Deyab, Carbohydr. Polym. 2011, 86, 1615.

[95] X. Wu, C. Lu, Z. Zhou, G. Yuan, R. Xiong, X. Zhang, Environ. Sci.: Nano 2014, 1, 71.

[96] Y.-C. Liu, T. C. Chuang, J. Phys. Chem. B 2003, 107, 12383.

[97] J. Han, L. Li, R. Guo, Macromolecules 2010, 43, 10636.

[98] C. Wang, N. T. Flynn, R. Langer, Adv. Mater. 2004, 16, 1074.

[99] J. Li, J. Xie, L. Gao, C. M. Li, ACS Appl. Mater. Interfaces 2015, 7, 2726.

[100] B. Song, K. He, Y. Yuan, S. Sharif-Asl, M. Cheng, J. Lu, W. A. Saidi, R. Shahbazian-Yassar, Nanoscale 2018, 10, 15809.

[101] T. Jain, S. Lara-Avila, Y.-V. Kervennic, K. Moth-Poulsen, N. Koeggaard, S. Kubatkin, T. Bjørnholm, ACS Nano 2012, 6, 3861.

[102] A. J. Mieszawska, G. W. Slawinski, F. P. Zamborini, J. Am. Chem. Soc. 2006, 128, 5622.