CONSPECTUS: Over the past 30 years, the engineering of plasmonic resonances at the nanoscale has progressed dramatically, with important contributions in a variety of different fields, including chemistry, physics, biology, engineering, and medicine. However, heavy optical losses related to the use of noble metals for the fabrication of plasmonic structures hindered their application in various settings. Recently, an answer to these long-standing issues emerged in the use of lattice plasmon resonances (LPRs, also called surface lattice resonances), bringing new excitement in the field of plasmonics. Specifically, the organization of plasmonic nanoparticles into ordered arrays enables far-field coupling of the scattered light exploiting the diffraction modes of the array, generating plasmonic resonances with bandwidths as narrow as a few nanometers, corresponding to an increase of over 10-fold in the quality factors compared to localized plasmon resonances. As such, LPRs offer new opportunities to harness light–matter interactions at the nanoscale, while generating renewed interest in the self-assembly of colloidal metal nanoparticles, as a scalable approach to the preparation of such plasmonic arrays. Templated self-assembly emerged as one of the most versatile approaches, being compatible with soft-lithographic techniques such as nanoimprint lithography and amenable to a variety of materials, colloids, and solvents. Templated self-assembly additionally allows the preparation of arrays where the repeating units are composed of multiple self-assembled nanoparticles (i.e., plasmonic clusters). In this system, near-field coupling can be finely tuned, thereby showing promising results in biosensing, catalysis, or plasmonic heating. In this Account, we review the preparation of ordered arrays of clusters of plasmonic nanoparticles. We present various aspects involved in the templated self-assembly of colloidal nanoparticles, with the aim of achieving at the same time close-packed structures within each cavity of the template, and uniform deposition over a large area. We then analyze the optical properties of the prepared substrates. The preparation of hierarchical structures and the possibility of tuning both the internal structure of the cluster and their organization into arrays with different lattice parameters enable control over both near-field and far-field plasmonic coupling. This unique feature of such substrates makes it possible to exploit the interplay between these two types of coupling, for the preparation of versatile functional substrates, expanding the possibilities for the integration of plasmonic arrays into functional devices for various applications. A well-established example is their use for surface-enhanced Raman scattering. On the other hand, optimization of far-field coupling provides access to plasmonic cavities for lasing or refractive index sensing. Despite two decades of fervid scientific research, the preparation and engineering of plasmonic arrays remains a relevant topic, and many directions remain largely unexplored. We conclude with a collection of perspectives and challenges that we find particularly stimulating toward future developments of the field.

1. INTRODUCTION

Understanding and controlling light–matter interactions has been a major driving force for many scientific breakthroughs with implications in the development of cleaner energy sources, faster communication systems, and a more sustainable future. The field of plasmonics investigates the manipulation of light–matter interactions at the nanoscale, by exploiting coherent oscillations of conduction electrons in (noble) metal objects, at the interface with a dielectric medium, a phenomenon called localized surface plasmon resonance (LSPR). LSPR excitation is accompanied by the following three phenomena: (i) generation of high-energy electrons (i.e. hot-electrons) that can intervene in chemical reactions; (ii) emergence of high electric field regions that affect optical phenomena via the Purcell effect; and (iii) relaxation of plasmon energy through photon–phonon coupling, generating heat toward the surrounding medium. All of these phenomena have found various applications, including catalysis, sensing, drug-delivery, and hyperthermia, while fueling research on the...
colloidal synthesis and assembly of plasmonic nanoparticles. Wet chemistry colloidal synthesis expanded exponentially during recent decades, achieving exquisite spectral LSPR tunability, from the ultraviolet (UV) to the far-infrared (IR),\textsuperscript{6,7} evolving from spherical nanoparticles into anisotropic shapes and chiral structures.\textsuperscript{8–10}

Another feature of plasmon resonances is their ability to couple and hybridize into new plasmon modes. When the gap between plasmonic particles is much smaller than the LSPR wavelength, interactions are dominated by near-field effects.\textsuperscript{11} As the coupling distance increases and becomes comparable to the resonance wavelength, far-field contributions prevail.\textsuperscript{12} A particular case of far-field coupling emerges when plasmonic nanoparticles are organized into ordered arrays, leading to the generation of surface lattice plasmon resonances (LPRs).\textsuperscript{13} A unique feature of LPRs is the possibility to engineer the resulting optical response by tuning geometrical parameters of the array, thereby extending the spectral window available for plasmonics with no need for modifying the nanoparticle building blocks.\textsuperscript{13}

Every dissipating mechanism has the undesired effect of damping plasmon resonances, ultimately affecting the propagation length of the electromagnetic wave along the surface, as well as its lifetime. Such effects are known as “optical losses”, which are described by the imaginary part of the permittivity of the metal at the plasmon frequency, and hinder quality factors in LSPRs (\(Q = \lambda/\Delta\lambda\), a parameter describing the damping rate of an oscillator/resonance), which rarely exceed 10 for individual nanostructures. When nanoparticles are organized in periodic lattices, light scattered in-plane by each repeating unit can interfere constructively with that from its neighbors, coupling in the far-field through the array’s diffraction modes.\textsuperscript{14} The resulting collective response can support spectral features with quality factors an order of magnitude higher than those in single nanoparticles.\textsuperscript{15} Ultranarrow LPRs were first reported by Kravets et al.,\textsuperscript{16} who demonstrated quality factors reaching 100 using ordered arrays of gold nanopillars over glass. Ordered plasmonic arrays are commonly fabricated by lithographic processes (\textit{e.g.} e-beam- or photo-lithography) and by thermal evaporation. Apart from long fabrication time and high cost, such approaches impose limitations on the morphology of the repeating units (which can only be modified in the \(x\)-\(y\) plane with a resolution of several nm), thus requiring \textit{ad hoc} optimization. Another limitation of lithographically fabricated arrays relates to surface chemistry, which can only be modified postfabrication. Both limitations can be overcome using colloidal nanoparticles as building blocks, allowing a high level of control over nanoparticle shape, composition, crystallinity, orientation, and surface chemistry, while reducing grain boundaries within individual nanoparticles, enabling a higher optical performance.\textsuperscript{17} The use of colloidalally synthesized nanoparticles enables modification of the internal structure of the repeating unit, which can be composed of single nanoparticles, dimers, or multiparticle clusters. More complex architectures create an intricate balance between near- and far-field coupling, leading to hot-spot engineering in combination with LPRs, an interesting perspective for plasmonic applications. However, the organization of such small objects into ordered arrays with sufficient precision turns out to be far from a trivial task.

Several self-assembly approaches have achieved large-scale organization,\textsuperscript{18} replication fidelity, and single nanoparticle manipulation,\textsuperscript{19} leading to self-assembly of various patterned materials.\textsuperscript{20} Reinhard and co-workers used poly(methyl methacrylate) (PMMA) masks fabricated by e-beam lithography, to template the ordered assembly of gold nanoparticles. Electrostatic interactions between colloidal particles and functionalized gold films as target substrates induced the formation of plasmonic clusters, with tunable interparticle and intercluster plasmon coupling.\textsuperscript{21} Larger assembly areas can be targeted using capillary-assisted particle assembly (CAPA), based on constraining nanoparticles inside cavities of a template by capillary forces at the three-phase contact line of a receding meniscus. Capillary-assisted assembly allows control at the single-particle level, by proper design of a template’s topography.\textsuperscript{22} However, similar to template-based dip \textsuperscript{4} or spin coating \textsuperscript{5} approaches, nanoparticles assemble inside template cavities and must be transferred to the substrate of choice using protocols such as transfer printing. Cortés et al.\textsuperscript{23} developed an improved strategy to obtain free-standing arrays of single gold nanoparticles using CAPA, followed by dissolution of a PMMA template. In another example, Gupta et al. used polydimethylsiloxane (PDMS) as a target elastomeric substrate, so that LPRs could be tuned by uniaxial stretching.\textsuperscript{24} Upon reversible mechanical deformation, the initial square lattice evolved into a rectangular pattern, and the
optical properties changed accordingly. Fery and co-workers developed a protocol based on wrinkled PDMS templates, in combination with the concepts introduced herein to study plasmon coupling between assembled nanoparticles.27 Where- as these techniques allow exquisite precision in nanoparticle positioning, template-assisted self-assembly has emerged as a promising one-step approach, achieving self-assembly upon drying a colloidal dispersion under confinement, with reusable templates. This methodology is extremely versatile and can be combined with nanoimprint lithography, thereby enabling compatibility with roll-to-roll fabrication and adaptability to different colloids, solvents, and surfaces.

This Account focuses on the fabrication, properties and applications of plasmonic superstructures obtained by template-driven assembly of gold nanoparticles. For more information about alternative approaches to colloidal self-assembly, we refer readers to recent reviews published on the subject.34 We first introduce template-assisted self-assembly, with particular emphasis on details to improve the control over the assembly process, together with a library of currently existing structures. We then describe the resulting plasmonic arrays, analyzing their optical properties, spectral tunability, and interplay between near-field and far-field effects. We finally present applications for different types of superlattices and conclude with our own view of particularly stimulating future directions.

2. TEMPLATE-ASSISTED SELF-ASSEMBLY

Template-assisted (or template-induced) self-assembly relies on prepatterned elastomeric molds to induce order from a colloidal dispersion (Figure 1). The core of the process comprises drop-casting and confinement of a small volume (typically few microliters) from a highly concentrated nanoparticle dispersion (i) between a template and a target substrate (ii). Solvent evaporation (iii) results in self-assembly of nanoparticles into superstructures replicating the size and shape of the template cavities, providing precise control on particle deposition over areas as large as square centimeters, while enabling nanoparticle self-assembly into close-packed structures. Upon drying, substrate and mold are gently separated (iv) to avoid disrupting the pattern.33 PDMS is usually the material of choice as the template, made by soft lithography replication of prepatterned surfaces (or masters).34 Nanoimprint lithography allows using the same PDMS molds to replicate the original surface by pressing and curing against photoresists, polymers, and other materials, over a virtually infinite number of times.35,36 These advantages render soft lithography compatible with roll-to-roll technologies and open the door to a more direct transfer into an industrial setup.

Optimization of templated self-assembly involves the combination of strategies acting on either of the three key elements of the process (colloid, patterned template, and substrate). These strategies can be classified in two major groups, toward achieving uniform large-scale organization while avoiding irregularities and defects that can hinder the optical performance of the system. We start by colloidal and surface-chemistry effects. Colloidal suspensions with a narrow dispersion in both size and shape are essential to achieve high-quality ordered structures, required to control the crystallinity of the assembly. Nanoparticles’ morphology and surface chemistry regulate interparticle interactions and colloidal stability, which in turn influence self-assembly under confinement. Similarly, particle–template and particle–substrate interactions affect the preferential adhesion of nanoparticles to either substrate or template, affecting the quality of the final product. Adhesion properties can be tuned through surface chemistry of both particles and substrate, solvent composition, and hydrophobicity/hydrophilicity of both surfaces. PDMS presents a soft hydrophobic surface, setting an initial contrast with glass or silicon substrates; simple hydrophilization of the target substrates via UV-ozone or oxygen/air-plasma treatments improves wettability and preferential adhesion of nanoparticles to substrates.

A second group of strategies targets convective flows, which influence the distribution of the colloid during solvent evaporation. Compared to a sessile drop, the drying mechanism is heavily influenced by the confinement between substrate and template. During evaporation, outward solvent radial flows can cause undesired accumulation of nanoparticles at the contact line, which is known as the coffee-ring effect (CRE) for sessile droplets. This effect must be suppressed to ensure homogeneous distribution of nanoparticles along the entire surface in contact with the patterned area. Different strategies can be introduced in the self-assembly protocol to hinder CRE. One example involves the modification of interparticle and particle–surface interactions, since a higher affinity to the substrate reduces CRE. Inward Marangoni flows, arising from surface tension gradients, have opposite effects to CRE and can also affect the spatial distribution of deposited nanoparticles.40 The concentrations of surfactants or other additives, the volume of drop-casted solutions, the use of a cosolvent, and again the choice of ligands can be used to balance such convective flows.

Altogether, an interplay between all these strategies enhances the versatility of the technique, whereas modifications of drop-casting and confinement can be used to adapt the method to specific colloid–substrate combinations. Useful variations include the introduction of a pre-evaporation (or aging) step prior to droplet confinement, or application of pressure by placing a weight on top of the PDMS template, to favor higher quality patterns. Scanning electron microscopy (SEM) characterization on different points of the sample is employed to assess the homogeneity and identify the effect of intertwined parameters, leading to precise control over self-assembly. Optimized templated self-assembly protocols can be used to prepare a wide range of nano- and microarchitectures over large areas within minutes. We provide below two examples of these strategies for optimized templated self-assembly of gold nanospheres and gold nanorods.

2.1. Template-Assisted Self-Assembly of Gold Nanospheres

The synthesis of uniform gold nanoparticles typically involves the use of cetyltrimethylammonium chloride (CTAC) as a surfactant. However, the dynamic adsorption of CTAC and formation of unstable bilayers requires replacement by a ligand forming well-defined coating shells, such as thiol-terminated poly(ethylene glycol) (PEG). As a result, colloidal stability is maintained at the high concentrations needed to build large-area assemblies using microliter-scale droplets, and affinity toward hydrophilized glass substrates is enhanced, minimizing undesired CRE. Hanske et al. used PDMS molds comprising arrays of inverted pyramids for the template-assisted self-assembly of PEG-coated gold nanospheres (Figure 2A). Inside template cavities, the nanoparticles assembled into highly ordered pyramidal supercrystals with face-centered cubic

https://doi.org/10.1021/accmater.1d00106
Acc. Mater. Res. XXXX, XXX, XXX–XXX
structure. Following the same principle, but using templates with smaller cavities, Matricardi et al. achieved square arrays of nanoclusters with submicron lattice parameters (Figure 2B). The concentration of the colloidal dispersion determined the amount of nanoparticles populating the patterned area. Insufficient or excessive concentrations translated respectively into the formation of partially empty patterns or a residual layer between clusters, meaning that nanoparticle concentration must be accurately tracked (e.g. by monitoring absorbance at 400 nm). The PEG coating on the nanoparticles ensured colloidal stability throughout the assembly process, whereas surfactants such as CTAC were used as additives to improve the quality of the assembly through combination of surface tension, surface charge, and depletion forces. For example, 50 μM CTAC was found to improve the homogeneity of gold nanosphere assemblies in water.41

2.2. Template-Assisted Self-Assembly of Gold Nanorods

When gold nanorods are used as building blocks, a shorter ligand is commonly used to replace cetyltrimethylammonium bromide (CTAB) and lower the surface charge. The amphiphilic (11-mercaptopoundecyl)hexa(ethylene glycol) (MUHEG or MUDOL) is known to induce preferential side-to-side nanorod interactions, leading to vertically aligned assemblies.45,46 Contrarily to CTAB, MUHEG promotes the Marangoni effect in sessile droplets,47 promoting accumulation of nanoparticles in the central area instead of the outer edges of the substrate. Hamon et al.45 demonstrated the self-assembly of MUHEG-coated nanorods into supercrystals with separations ranging from 20 μm to 700 nm. Further miniaturization into the nanometer scale was found to be more challenging. Precise control over the distribution of nanorods was achieved by Hanks et al.,44 using ethanol as a cosolvent to improve template wetting and achieve kinetic control over nanorod self-assembly (Figure 2C). A pre-evaporation step prior to confinement resulted in two complementary effects occurring in the sessile drop. On one hand, ethanol removes adsorbed CTAB molecules from the interface of MUHEG-coated nanorods, hindering colloidal stability. On the other hand, fast ethanol evaporation and a transient interplay between solute- and surfactant-driven Marangoni flows promote a gradual agglomeration of nanorods at the droplet surface (Figure 3A). The duration of this pre-evaporation process affects the mobility of the nanoparticles and translates into different degrees of substrate filling (Figure 3B). Optimal evaporation times provided kinetic control over the resulting nanoparticle concentration inside the patterned area (Figure 3C–E). If the dispersion was confined at early stages of pre-evaporation, CRE dominated the distribution of nanoparticles upon drying. Excessively long evaporation times would lower ethanol concentration, reverting agglomeration at the drop surface and promoting CRE. Modification of the initial concentrations of CTAB and nanorods in the dispersion affected the presence of nanoparticles inside the mold cavities, higher concentrations leading to taller self-assembled structures, and promoting a more accurate reproduction of the template morphology (Figure 3F, G). The use of ethanol as cosolvent can also be implemented for PEG-coated spheres, with better control over self-assembly and avoiding the substrate hydrophilization step.

3. OPTICAL PROPERTIES OF PLASMONIC SUPERLATTICES

A complete theoretical description of LPRs is beyond the scope of this Account, we refer the reader to excellent reviews on the subject.13–15 We do provide a brief overview, focusing on the most relevant aspects (and equations) required to correctly interpret the extinction profiles of plasmonic arrays. Lattice plasmon resonances emerge when diffracted orders from a two-dimensional (2D) grating (Rayleigh–Wood anomalies)48,49 spectrally overlap with LSPRs of the repeating units.50 This periodic configuration has two important consequences: (i) the overall response of the array compensates damping in individual particles, leading to remarkably narrow plasmon resonances, down to few nm,51 and (ii) the diffractive component allows the spectral tuning of LPRs through simple modifications of geometrical parameters. To better understand the optical response of these systems, one should be able to predict the position of the diffraction lines with respect to the LSPR of the repeating unit. We first examine the diffraction component alone. Rayleigh–Wood anomalies arise when the diffracted modes of a grating evolve from evanescent to propagating. The spectral position of such anomalies (λ_{HW}) can be predicted by applying conservation of momentum and Bragg condition at the grating interface, leading to the following equation:

\[ n_{\text{eff}} \lambda_{\text{HW}} \approx n_{\text{LSPR}} \lambda_{\text{LSPR}} \]
Where, $n_{\text{medium}}$ is the refractive index around the grating, $\Lambda_x$ and $\Lambda_y$ are the lattice parameters of the grating, $\theta$ is the illumination angle, $q$ is a factor related to the diffraction order under examination, and $l$ and $m$ are signed integers referring to diffraction orders. Equation 1 shows how the diffraction modes of the grating can be modulated by modifying the illumination geometry. This equation can be simplified further

$$\lambda_{\text{RW}} = \frac{\Lambda_x y}{q} (n_{\text{medium}} \pm \sin \theta), \quad \text{with} \quad q = \sqrt{m^2 + l^2}$$

in the common case of a square array ($\Lambda_x = \Lambda_y$), under normal illumination with scrambled polarized light ($\sin \theta = 0$), considering only the first diffraction order ($\pm 1$) and $q = 1$. This simple equation is very useful, as it can readily predict the spectral position of LPRs under normal incidence. In this Account, we analyze the case of 2D plasmonic arrays. The angular dependence of the diffraction lines is more complicated than that in eq 1, as both illumination ($\theta$) and azimuthal ($\phi$) angles must be measured to correctly predict the position of Rayleigh–Wood anomalies, for which we use the following set of equations:

$$\lambda_{\text{RW}} = \Lambda \cdot n_{\text{medium}}$$

Rayleigh-Wood anomalies occur when $\cos (\theta_{\text{def}})$ passes through zero (i.e. it is tangential to the grating). It is important to mention that LPRs are surface modes that remain confined at the grating interface. When the refractive index at the interface is asymmetric (i.e. the refractive index of superstrate and substrate differ, as for the case of nanoparticles deposited on glass and surrounded by air), the scattered light will radiate predominantly in the highest refractive index media (typically the substrate), drastically reducing in-plane coupling with the grazing diffraction modes. This results in loss of coherence of the LPR and broadening of the spectral features, especially when the plasmonic repeating units are smaller than $\Lambda$. Consequently, a superstrate with an appropriate refractive index is often applied to the plasmonic array, e.g. by coating a
Figure 4. Structural and optical characterization of plasmonic arrays with varying lattice parameter \( \Lambda \). (A) Normalized extinction spectra of square plasmonic arrays with different lattice parameters: \( \Lambda = 200 \) (black line), 300 (red line), 400 (blue line), 500 (green line), and 600 nm (purple line). The dotted vertical lines mark the position off the Rayleigh Wood’s anomalies. (B–C) Contour plot showing the evolution of the extinction profile as a function of the illumination angle (\( \theta \)) for \( \Lambda = 200 \) (B) and 400 nm (C). (D) Extinction spectrum of a \( \Lambda = 400 \) nm square array illuminated at a \( \theta = 37^\circ \). The dotted vertical line marks the position off the Rayleigh Wood’s anomaly. (E–F) Scanning electron microscopy images of square plasmonic arrays with different \( \Lambda \): 200 (E), 300 (F), 400 (G), 500 (H), and 600 nm (I). The color code is the same as that used in panel A (Reproduced with permission from ref 38. Copyright 2021 Wiley-VCH).

Now that we can predict the position and angular dependence of the diffraction modes, we can also analyze their interaction with plasmonic modes. When the grating is composed of plasmonic units, the emergence of LPRs can be described in the framework of coupled-dipole approximation theory, where each nanoparticle (with position \( r_i \) and polarizability \( \alpha_i \)) is represented by an electric dipole.\( ^{34} \) The electric field “felt” by each of the \( N \) nanoparticle positions will be a combination of the incident field and the retarded electric fields produced by the other \( N - 1 \) nanoparticles (dipoles). In other words, the induced dipole \( p \) (and consequently the extinction cross-section) of each nanoparticle can be evaluated by correcting the response to the external field for the interactions with each of the other dipoles in the system. These interactions can be combined into a single dipole, named dipole sum, \( S \). In the specific case of a 2D periodic array, the dipole sum will also be periodic, and the mathematical treatment can be simplified to the following equation:

\[
P = \frac{E_0}{1/\alpha - S}
\]  

(4)

Quick examination of eq 4 helps us draw important conclusions regarding the optical response of plasmonic arrays. First, the presence of the polarizability \( \alpha \) suggests how, in analogy with LSPRs, LPRs can be tuned by modifying the plasmonic repeating unit (shape, composition, orientation with respect to the incident wave). However, the presence of the dipole sum marks a clear difference between both types of resonances. In fact, \( S \) varies with geometrical parameters of the array such as the lattice constant \( \Lambda \) and its geometry, or the size of the repeating unit, thereby providing alternative ways of tuning the overall plasmonic properties, as compared to LSPRs. For example, by reducing the symmetry of the array (e.g., rectangular pattern), one can introduce a polarization dependent response.\( ^{35,36} \) Moreover, the conditions for the generation of an LPR can be found by minimizing the denominator of eq 4, showing how LPRs are generated when the inverse of the polarizability of one of the nanoparticles in the array is compensated by \( S \). It is important to remember that these conditions do not correspond to any LSPR maximum, as they do not identify a polarizability pole. It is found mathematically that these new resonance conditions are achieved for wavelengths corresponding to Rayleigh–Wood anomalies, when the evanescent diffracted field propagates along the array and can couple with the scattered field of the nanoparticle LSPRs.\( ^{37} \) In other words, diffraction modes enable and promote the interaction between neighboring particles, maximizing far-field coupling between the plasmonic repeating units of the array. Hybridization with different lattice modes has also emerged as a way to tune the optical response of the system.\( ^{38} \) One of the advantages of far-field coupling is that it decays with the inverse of the distance (1/\( d \) instead of 1/\( d^3 \), characteristic of near-field interactions). Since the array extends in both \( x \) and \( y \) directions, the number of dipoles added to the far-field interaction scales with the second power of distance, effectively compensating for the decay of far-field coupling, resulting in a significant narrowing of the LPR linewidth. In most supercrystals produced by template-induced assembly, single nanoparticles are replaced by more complex repeating units such as clusters or meta-molecules,\( ^{38,39} \) in which both near- and far-field coupling modify the electric field distribution. Near-field coupling concentrates intense electric fields within small volumes (hot spots), whereas far-field coupling typically shows more moderate values of the electric field in a more extended region, farther away from the metal surface.\( ^{37} \) The theoretical framework presented above becomes extremely helpful to navigate such more complex systems and to correctly investigate and interpret their far-field optical...
response (Figure 4). As a practical example, we examine the case of square lattices ($\Lambda = y$) with a PDMS index-matching layer ($n_{\text{medium}} = 1.45$), and focus on the first diffraction order ($q = 1$). We thus simplify eq 2 into $\lambda_W = 1.45\Lambda$, and the LPRs for lattice pitches of 200, 300, 400, 500, and 600 nm can be predicted to position around 290, 435, 580, 725, and 870 nm, respectively. As can be seen in Figure 4A, the diffraction lines do not match to any extinction maxima. This is because far-field coupling is influenced by the localized response of the clusters. A larger cavity translates into bigger cluster dimensions (Figure 4E−I), causing LSPR red-shifting and broadening. In all cases, the diffraction lines are blue-shifted with respect to the plasmonic response, generating asymmetric extinction profiles where maxima do not necessarily correspond to a LPR.

In order to correctly identify LPRs, one of the easiest experimental approaches is to take advantage of the dependence of Rayleigh−Wood anomalies on illumination angle (Figure 4B, C). Equations 3a, b can be used to predict the angular dependence of the diffraction lines (white solid lines in Figure 4B, C). The same behavior should be observed for LPRs, whereas LSPRs are not influenced by the illumination angle, allowing a clear identification of the nature of each extinction maximum. Let us compare two different cases: For $\Lambda = 200$ nm (Figure 4B), Rayleigh−Wood anomalies do not overlap with the clusters’ LSPR, even for high illumination angles (up to $40^\circ$). Consequently, no conditions are fulfilled for LPR generation, and the extinction profile of the system is purely localized, remaining angle-invariant. On the contrary, when $\Lambda = 400$ nm (Figure 4C), the contour plot clearly shows a red-shift of the anomalies that hybridize with the LSPR of the array, starting from an illumination angle $\theta = 25^\circ$. Figure 4D shows the extinction spectrum for $\theta = 37^\circ$, where the sharp feature at 810 nm marks the emergence of an LPR.

Colloid-based templated self-assembly offers the possibility to build supercrystals from a wide variety of colloids, thereby tailoring their optical response. For example, by varying the size of gold nanospheres different degrees of near-field coupling within the clusters can be achieved, with important consequences on the extinction profile of the array (Figure 5). When gold clusters are made of larger spheres (>40 nm in diameter), strong near-field coupling within the clusters creates spectrally broad plasmon resonances, characterized by a large number of intense hot-spots (Figure 5A, B). The collective response of the array in the far-field is then unable to efficiently compensate for optical losses within the clusters, thus limiting the associated quality factors (Figure 5C). In other words, the optical response of the system is dominated by the LSPR in each cluster, over the LPR of the plasmonic array. One way to minimize the influence of near-field coupling within the clusters comprises the use of smaller nanoparticles, <25 nm in diameter (Figure 5D, E), resulting in blue-shifted and narrower LSPRs. This facilitates engineering of mode hybridization with the first order diffraction mode, obtaining sharp LPRs with much higher quality factors (Figure 5F), which is a requirement for optical applications such as lasing or amplification of nonlinear phenomena. Another possible explanation for the improved quality factors obtained for smaller gold colloids is the reduced structural variability within clusters at each lattice point. Theoretical predictions however

Figure 5. Role of the near-field. Simulated electric field distribution (A, D) of plasmonic square arrays ($\Lambda = 400$ nm), varying the gold nanoparticle size: S4 (A) and 11 nm (D). (B, E) Scanning electron micrographs of square arrays ($\Lambda = 600$ nm) prepared from gold nanoparticles of S4 (B) and 23 nm (E). (C, F) Extinction profiles of plasmonic arrays prepared using S4 (C) and 23 nm (F) nanoparticles: $\Lambda = 400$ (black line), 500 (red line), and 600 nm (blue line) (Reproduced with permission from ref 38. Copyright 2021 Wiley-VCH).
show that the contribution to LPR narrowing is only minor.\textsuperscript{38} On the other hand, these structural defects have major implications on the lattice response of single nanoparticle plasmonic arrays.\textsuperscript{60} Consequently, although the sharpest resonances have been observed so far in single-particle plasmonic arrays,\textsuperscript{22,61} from a colloidal self-assembly perspective, the production of arrays using small nanoparticles is a simpler approach for the preparation of high quality factor resonances.

4. APPLICATIONS

In the previous section, we showed that particle size dictates the optical properties of plasmonic supercrystals, with important implications in the preparation of substrates targeting different applications. Whereas larger particles are the preferred choice toward plasmonic arrays with strong near-field coupling, with applications in sensing, catalysis, or plasmonic heating, small-particle plasmonic supercrystals can lead to plasmonic cavities for lasing or refractive index sensing. In what follows, we illustrate some uses of supercrystals produced by template-induced assembly.

4.1. Surface-Enhanced Raman Scattering

Surface-enhanced Raman scattering (SERS) relies on enhanced local fields to boost the Raman signal of molecules adsorbed on plasmonic surfaces. High electric fields associated with plasmonic resonances lead to enhancement factors as high as 10\textsuperscript{10}, reaching single-molecule detection limits.\textsuperscript{62} Similar detection schemes have been extended to LPRs. The organization of plasmonic building blocks into ordered superlattice arrays enables tuning the optical response of the assembly, thereby maximizing the enhancement factors at selected excitation wavelengths, using both gold nanorods and nanospheres (Figure 6A, B).\textsuperscript{36,44} Additionally, far-field coupling modifies the electric field distribution within the array, so that regions of highest electric field enhancement extend farther away from the surface of the repeating unit, thereby improving the limit of detection.\textsuperscript{36}

The high SERS efficiency of plasmonic superlattices allows implementing more realistic and complex biodetection schemes.\textsuperscript{63} The potential of this material has been recently demonstrated for real-time and label-free detection of relevant tumor metabolites, such as tryptophan and purine derivatives, which provide information about tumor development. Analysis of the extracellular environment demonstrated the possibility of monitoring kynurenine and tryptophan levels via their intrinsic SERS signals (Figure 6C). The concentrations of these metabolites are regulated by the indoleamine 2,3-dioxygenase 1 (IDO-1) enzyme, which is overexpressed in various tumor cell types, and catalyzes the conversion of tryptophan into kynurenine. The analysis was further performed \textit{in situ} using a hydrogel-based three-dimensional cancer model, which more closely recreates the biochemical and biophysical factors in the tumor microenvironment.\textsuperscript{63} The use of LPR-SERS sensing to monitor enzymatic activity in tumor cells can help illuminate their function, identify new biomarkers, and test different treatments. A drawback of the near-field nature and high sensitivity of SERS detection schemes is the so-called “memory effect”, i.e. the uncertainty introduced in real-time SERS measurements due to irreversible adsorption of chemical species onto the plasmonic surface used to enhance the signal. To overcome this limitation, Plou et al. used an impermeable poly(lactic coglycolic acid) (PLGA) sheathing layer, which prevents undesired adsorption on the plasmonic substrate.\textsuperscript{64} At a selected time, a measurement

![Surface enhanced Raman scattering](image)

![Label-free real-time monitoring of Tumor activity](image)

**Figure 6.** SERS detection with plasmonic arrays. (A, B) Surface enhanced Raman scattering signal as a function of the lattice parameter for plasmonic arrays of gold nanospheres (A) and gold nanorods (B). The SERS intensity correlates with the spectral match between the lattice plasmon and the excitation laser. (C) SERS spectra of HeLa cell supernatants with varying interferon-gamma (IFN-\textgamma; for activation of IDO-1 expression) and tryptophan concentrations, tracking both kynurenine (orange) and tryptophan (green). (D) Scheme of the real-time detection in bioreactors by combination of plasmonic superlattices with silicone chambers containing HeLa cells. \textit{In situ} SERS measurements using a thermolabile poly(lactic coglycolic acid) (PLGA) layer account for the interconversion of adenosine (pink) into hypoxanthine (blue) after 24 h, in agreement with a control made by extracting the supernatant, and thus overcoming the memory effect in a substrate without PLGA (Reproduced with permission from refs 36 (A), 44 (B), 63 (C), and 64 (D). Copyright 2018, 2019, and 2021 American Chemical Society and 2020 Wiley-VCH).
plasmonic units. Further extension of the technique to different plasmonic materials will expand the accessible wavelengths by LPRs, from the UV (aluminum, silver), to the deep IR (copper, doped oxides). Incorporation of optically active nanoparticles as building blocks in template-assisted assemblies would also be a promising direction to expand the horizons of colloidal plasmonic chirality, which has recently witnessed tremendous advances. Moreover, templated self-assembly can be adapted to the assembly of nonplasmonic colloids, as was demonstrated for perovskite nanocrystals, including dielectrics (mesoporous silica or titania), magnetic nanoparticles (iron oxide), or other emitters (quantum dots or carbon dots). These studies will also open the possibility to coassemble various types of colloids, creating interesting solutions for plasmonic/chirality applications avoiding thermal evaporation and complex lithography. As we have seen in section 2, controlling the near-field coupling within the repeating unit would open completely new research avenues, targeting applications in strong-coupling interactions, catalysis, biosensing, and metamaterials. In this context, the versatility offered by the use of colloidal building blocks represents an incredibly strong asset, which will thrust new efforts in the use of templated self-assembly for the preparation of ordered nanoparticle arrays.

5. FUTURE DIRECTIONS

We believe we have only scratched the surface of what templated self-assembly can offer for the fabrication of ordered nanoparticle arrays. This versatile technique is compatible with many materials, offering an opportunity for the seamless integration of plasmonic architectures in various technologies. The experience gathered from different self-assembly systems opens possibilities toward fabrication of even more unconventional morphologies, with high potential for metamaterial applications avoiding thermal evaporation and complex lithography. Different colloids and patterned geometries on PDMS molds may unlock exciting optical properties not exploited so far. For example, the possibility to control the height of the assembly through nanoparticle concentration may enable exploitation of subradiant out-of-plane resonances in plasmonic arrays. 31 In another example, swelling of the PDMS template by infiltration of organic solvents can be exploited for controlled pattern deformation.66 A deeper understanding of the drying mechanism would enable to control convection of the solvent at the perimeter of the cavity space, inducing a local CRE, which can be exploited to form arrays of ring-shaped plasmonic units. Further extension of the technique to different plasmonic materials will expand the accessible wavelengths by LPRs, from the UV (aluminum, silver), to the deep IR (copper, doped oxides). Incorporation of optically active nanoparticles as building blocks in template-assisted assemblies would also be a promising direction to expand the horizons of colloidal plasmonic chirality, which has recently witnessed tremendous advances. Moreover, templated self-assembly can be adapted to the assembly of nonplasmonic colloids, as was demonstrated for perovskite nanocrystals, including dielectrics (mesoporous silica or titania), magnetic nanoparticles (iron oxide), or other emitters (quantum dots or carbon dots). These studies will also open the possibility to coassemble various types of colloids, creating interesting solutions for plasmonic/chirality applications avoiding thermal evaporation and complex lithography. As we have seen in section 2, controlling the near-field coupling within the repeating unit would open completely new research avenues, targeting applications in strong-coupling interactions, catalysis, biosensing, and metamaterials. In this context, the versatility offered by the use of colloidal building blocks represents an incredibly strong asset, which will thrust new efforts in the use of templated self-assembly for the preparation of ordered nanoparticle arrays.

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Figure 7. Two-photon absorption enhancement in CsPbBr3 photonic crystals. (A, B) Scanning electron microscopy characterization of self-assembled perovskite nanocrystals into large-area 2D photonic crystals (A) with cubic close-packed order (B). (C) Extinction spectra of flat films (green line) and photonic crystals with 400, 500, and 600 nm lattice parameters (blue, black, and red lines, respectively). (D) Fluence-dependent photoluminescence of CsPbBr3 nanocrystals self-assembled into 2D photonic crystals with a lattice spacing of 600 nm, under fs laser excitation at 800 nm. (C and D, insets) Photographs of the perovskite photonic crystals showing diffraction (C) and waveguiding (D) under white light illumination and laser excitation, respectively (Reproduced with permission from ref 28. Copyright 2020 Wiley-VCH).
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Notes
The authors declare no competing financial interest.

Biographies
Leonardo Scarabelli is hosted as a "La Caixa" Junior Leader in Dr. Mihi’s group at the Institute of Materials Science of Barcelona (ICMB-CSIC) since 2019. He obtained his Ph.D. from the University of Vigo in 2016, followed by a postdoc at the University of California, Los Angeles. His research focuses on ordered arrays of colloidal plasmonic nanoparticles for the study of light–matter interactions in the strong-coupling regime.

David Vila-Liarte received his B.S. and Master’s degrees in nanoscience and nanotechnology from the Autonomous University of Barcelona (2019). During this time, he worked on the template-assisted self-assembly of gold nanorods and implemented the technique on perovskite nanocrystals in Dr. Mihi’s group. In 2019 he joined Prof. Liz-Marzán’s lab as a Ph.D. student, focusing his research on plasmonic chirality.

Agustín Mihi obtained his Ph.D. in Physics in 2008 from the Institute of Materials Science of Seville (ICMS-CSIC). He was honored with a Beckman postdoctoral fellowship at the University of Illinois in Urbana–Champaign (USA) and a Marie Curie cofund fellowship at the Institute of Photonic Sciences (ICFO). Since 2018, he has been a tenured researcher at the Institute of Materials Science of Barcelona (ICMAB-CSIC) working on scalable photonic nanostructures for optoelectronics.

Luis M. Liz-Marzán has been Ikerbasque Professor and Scientific Director of CIC biomaGUNE since 2012. He graduated in Chemistry from the University of Santiago de Compostela and was a postdoc at Utrecht University and a Professor at the University of Vigo (1995–2012). Liz-Marzán works on colloidal synthesis and self-assembly of metallic nanocrystals, as well as the characterization and application of their plasmonic properties. His recent research focuses on the biomedical applications of plasmonic nanostructures.

ACKNOWLEDGMENTS
This project has received funding from the Spanish Ministerio de Ciencia e Innovación through grants PID2019-106860GB-I00 and FUNFUTURE (CEX2019-000917-S), in the framework of the Spanish Severo Ochoa Centre of Excellence program, as well as MDM-2017-0720 grant to CIC biomaGUNE. The research of L.S. is supported by the 2020 Maeztu Units of Excellence Program from the Spanish State Council (ERC AdG 787510, 4DbioSERS) and the Maria de Maeztu Foundation (ID 100010434, fellowship code LCF/BQ/PI20/15, 2751–2755).

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