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The rich photonic world of plasmonic nanoparticle arrays

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Metal nanoparticle arrays that support surface lattice resonances have emerged as an exciting platform for manipulating light–matter interactions at the nanoscale and enabling a diverse range of applications. Their recent prominence can be attributed to a combination of desirable photonic and plasmonic attributes: high electromagnetic field enhancements extended over large volumes with long-lived lifetimes. This Review will describe the design rules for achieving high-quality optical responses from metal nanoparticle arrays, nanofabrication advances that have enabled their production, and the theory that inspired their experimental realization. Rich fundamental insights will focus on weak and strong coupling with molecular excitons, as well as semiconductor excitons and the lattice resonances. Applications related to nanoscale lasing, solid-state lighting, and optical devices will be discussed. Finally, prospects and future open questions will be described.

Introduction

Nanophotonics encompasses the manipulation of light at the nanoscale and has flourished in the past two decades because of a confluence of integrated advances in materials, nanofabrication, and modeling [1]. In particular, plasmonics, the resonant interaction of light with metals [2,3], has driven much of the recent attention because of unprecedented optical properties and a wide range of unique applications [1,4,5]. Starting with the early work of Michael Faraday on gold nanocolloids [6] and stained glass windows in medieval churches [7], the beautiful colors produced by “finely-divided” gold and other metal nanoparticles have been of high interest. Metal nanoparticles (NPs) exhibit localized surface plasmon (LSP) excitations, coherent oscillations of free electrons [8–10] whose optical response can be tailored by size, shape, and materials of the nanostructures [11,12]. LSPs can lead to large local electromagnetic field enhancements in deep sub-wavelength volumes [13]; if the NPs are in very close proximity, their near-fields can couple and further confine the fields [14,15]. The properties of these nearly touching NPs have been used in a wide range of applications from spectroscopy to sensing and catalysis [16–19].

Compared with individual and small clusters of NPs, metal particles—organized into ordered arrays with spacings comparable to the wavelength of light—can produce even greater field enhancements and higher quality resonances by exploiting short and long-range interactions [20]. Long-range (radiative) coupling between LSPs of single NPs can be mediated by two classes of photonic modes: diffraction modes in the plane of the array [21–28] and guided modes in supporting dielectric slabs [29]. Diffraction-mode coupling requires a uniform dielectric environment around the metal NPs to produce surface lattice resonances (SLRs, also called lattice plasmons), while guided-mode coupling generates waveguide polaritons or quasi-guided modes. The primary reason why SLRs have gained prominence is their...
combination of desirable plasmonic and photonic attributes: high field enhancements characteristic of plasmonic nanostructures extended over large volumes with long-lived lifetimes from the photonic array structure. All-dielectric NP arrays have been reviewed recently [30,31] and exhibit properties that complement those of SLRs.

In this Review, we summarize the recent advances in plasmonic NP arrays and offer prospects for future emerging applications. First, the general design principles of NP array characteristics and corresponding linear optical properties will be established. Different classes of SLRs will be described by experiment and theory. Second, weak and strong coupling regimes between organic dye molecules and SLRs will be reviewed. Third, the use of SLRs as optical feedback for entirely new classes of nanoscale lasers will be discussed. Fourth, interactions between electronic materials and SLRs will be compared with those in organic dyes. Finally, broad applications of SLRs from sensing to solid-state lighting will be introduced.

Linear optical properties of nanoparticle arrays
Sample preparation
High-quality SLRs require an optimized combination of NP unit cells and lattice geometry. Direct-write methods such as electron-beam lithography [23] are advantageous to design arbitrarily shaped nanostructures and were the first approaches to produce NP arrays that could support SLRs [23,28]. Serial processes, however, have challenges in scaling array areas and overall production costs, which have limited widespread dissemination and new applications. Parallel nanofabrication methods that use poly(dimethylsiloxane) (PDMS) stamps such as PEEL (Photolithography + E-beam deposition + Etching + Lift-off) and Surface Conformal Imprint Lithography (SCIL) have opened opportunities to generate large-area (>10 cm²) arrays of NPs. In PEEL, free-standing metal thin films perforated with nanoholes [32] function as physical deposition masks to create NP arrays in a range of materials and shapes determined by the hole mask (Fig. 1a). Fig. 1b is a SEM image of Au nanohole array film partially peeled off from Al NP arrays. Fig. 1c is an optical image of typical areal sizes (>cm²) of NP arrays produced by PEEL. This masking method can also be extended to create NP superlattices with microscale arrays of finite arrays of NPs (patches) [33]. In SCIL, flexible stamps are used to replicate the lattice pattern in sol–gel on a substrate. This pattern combined with metal deposition and lift-off can produce wafer-scale arrays of metal NPs [34].

Tuning the optical response for a fixed set of NP array parameters can be achieved by changing the refractive index environment [35,36] or by patterning NPs into mechanically stretchable materials such as PDMS [37]. Most SLR studies have focused on NP arrays made from Au and Ag because of their strong optical responses over the visible and near-infrared (NIR) wavelengths; arrays made from Al, however, have recently been shown to support lattice resonances with very high quality over the entire UV to NIR range [34,37–39]. Fig. 1d–f highlight different NP shapes, from NP dimers [26,40] to cylindrical NPs [35] to nanorods [41] whose arrays have produced SLRs. The ultra-narrow resonances (down to a few nm in experiments [35,42]) can be dipolar [26–28,33,35,37,43] or quadrupolar [37,40,44] in character depending on the geometric properties of the NPs and their coupled diffraction mode order.

Theory of strongly coupled nanoparticle arrays
Many years before strongly coupled NP arrays could be realized experimentally, Markel [45] Carron, [46] and Schatz [21,22,24,25] predicted SLRs and provided design rules regarding how to optimize the ultra-narrow (<1 nm) linewidths. The coupled dipole approximation (CDA) is most often used to
understand the coupling between NPs in arrays, where each particle is treated as a single-dipole resonator with polarizability $\alpha_{NP}$ depending on material, size, and shape [28]. At resonance, all NPs oscillate in phase and reside in the antinodes of the standing wave formed in the plane of the lattice. Because diffractive scattering of photons by each NP can excite the LSPs of adjacent NPs instead of decaying into free space, the lattice resonances suppress radiative loss. Assuming the induced polarization in each NP is the same, the effective array polarization can be treated as the sum (S) of the incident and radiated fields from all other dipoles in the array. When the real part of $(1/\alpha_{NP} – S)$ vanishes, the imaginary part of the dipole sum is also reduced, and then a narrow resonance peak arises in the extinction spectra. The SLR condition only exists at the longer wavelength side of the diffraction mode where constructive interference results in a standing wave across the NPs [21,28]. Further analytical details and discussion can be found in Refs. [47] and [48].

For larger NPs that support higher order plasmon modes (beyond dipolar modes) [49], the CDA cannot accurately capture the physics; however, a model that considers NPs as electric dipole and quadrupole independently can resolve this issue [50]. The discrete dipole approximation, where NPs are represented by polarizable cubes that include higher order excitations, can also predict lattice resonances with higher order modes [51]. Besides analytical models, numerical methods such as finite-difference time-domain (FDTD) [52] approaches and finite element methods (FEMs) [53] solve Maxwell’s equations on a meshed grid and can generate not only far-field spectra but also near-field properties such as phase, field intensity, and charge distribution of the electromagnetic field components. This near-field information is critical to identify the origins of the SLR excitations.

Different classes of surface lattice resonances

Dipolar lattice resonances

Fig. 2a highlights SLRs from a 2D square Au NP array ($d=120$ nm, $p=600$ nm) that exhibits very narrow linewidths (3–4 nm; quality factor $Q = \lambda/\Delta\lambda$ of ~200) at normal incidence ($\theta = 0^\circ$). Like other plasmonic nanostructures [12], NP arrays that support lattice resonances are sensitive to changes in refractive index. At higher indices, the SLR shifts to longer wavelengths, and at lower indices, the resonance shifts to shorter wavelengths [35]. Although the optimal SLRs result when the superstrate and substrate are index matched [54], the collective lattice modes are tolerant to small mismatches ($\Delta n \sim 0.05$) [35]. From FDTD simulations, at $\theta = 0^\circ$ or zero in-plane wavevector ($k = 0$), the near-field regions around the NPs show a characteristic dipolar pattern with enhancements two to three orders of magnitude larger than the incident light, concentrated at opposite sides of NPs in the direction of polarization (Fig. 2b). The neighboring NPs oscillate with the same phase and form a standing wave across the lattice perpendicular to the polarization (Fig. 2c).

SLR modes can have either in-plane or out-of-plane character depending on NP geometry. The primary factor determining in-plane dipolar lattice modes is NP diameter [35,37]. For example, as 2D square NP diameter decreased from 120 nm to 60 nm, the LSP of the individual NPs blue-shifted toward a diffraction mode, and hence the SLR linewidth dropped from 30 nm to 5 nm ($Q \sim 108$). Out-of-plane dipolar modes can be tuned by controlling NP height after exceeding a minimum height [43].
NPs with similar diameters and heights >100 nm, both in-plane and out-of-plane dipolar LSPs coupled to the array structure, resulting in a Fano resonance within a broad resonance background [43]. The sharp resonance was associated with the off-plane component and sensitive to changes of NP height, while the broad resonance peak was from the in-plane component.

**Quadrupolar lattice resonances**

Progress in the fabrication of larger NPs such as rods [44] or cylinders [37] has made possible the observation of high-order SLRs. Because of their net zero dipole moment, quadrupolar resonances can only weakly interact with light (i.e. they are “dark” in optical far-field measurements) and are rarely observed [55,56]. In arrays of long Au rods (L = 420 nm), in-plane quadrupolar coupling between NPs can produce narrow resonances on a dipole background. The sub-radiant (dark) character led to a much higher Q (~700) compared with radiant (bright) counterparts [44]. In contrast, for arrays of cylindrical Al NPs (d ≥ 120 nm), out-of-plane quadrupole lattice resonances can be excited along with in-plane dipolar lattice plasmon modes [37] but with very different qualities (Fig. 2d). To optimize the out-of-plane quadrupole lattice modes, the dipolar LSP must be detuned from the diffractive coupling condition. The electric near-field intensity and charge distribution of a quadrupolar SLR (Fig. 2e and f) show distinct characteristics different from those of dipolar SLRs.

Unit cells composed of NP dimers offer an alternative method to induce multi-polar resonance coupling in arrays [24] since the hot-spot intensity in the gaps depends on polarization. Interestingly, in arrays of asymmetric disc dimers [40], the plasmon modes can hybridize and produce two different modes with dipole moments on adjacent NPs either in-phase or out-of-phase with each other. The broken symmetry of the dimers introduced radiative coupling of the dark mode to free-space light. The dark mode related to the SLR exhibited one sharp resonance in addition to the one associated with the bright mode. Unlike quadrupolar SLRs in long nanorods that were not observed under normal incidence light, the asymmetric NP dimers sustain a non-vanishing net dipole moment and do not require oblique excitation to provide additional momentum for coupling to the far field.

**Superlattice plasmons**

Lattices with hierarchical microscale structure (arrays of patches) can support extremely high-order diffractive mode coupling because of the microscale periodicity (10–25 μm) [33]. Superlattice SLRs can be significantly narrower than finite-area NP arrays (patches) and exhibit stronger local fields. When shape and size of the NP units are kept constant, superlattice SLRs showed a line-width reduction from 35 nm to 3 nm, and the localized near-field enhancement around the NPs increased from 10- to 40-fold depending on patch–patch spacing. Separation between superlattice SLRs can be tuned by the Bragg modes defined by the microscale periodicity. Compared with SLRs from single-lattice arrays, superlattice SLRs share the same dominant modes (although scattering orders are different) with new satellite resonances at longer wavelengths with separations up to 120 nm.

**Dispersion diagrams of coupled nanoparticle arrays**

One significant advance resulting from the fabrication of macro-scale areas (>cm²) of NPs is the construction of dispersion diagrams out to very high angles. Different from LSP resonances in isolated particles, SLRs from NP arrays are dispersive because their photonic diffraction mode components are determined by array periodicity and the surrounding refractive index [30]. Samples illuminated with collimated white light under transverse magnetic (TM) or transverse electric (TE) polarization at different incident angles can result in a wavelength vs. angle (θ) map (Fig. 3a and b) that can also be plotted as an energy vs. in-plane wavevector (k) dispersion diagram (Fig. 3c and d). Under TM-polarized light, the dispersion of SLRs from 2D square arrays of cylindrical Au NPs follows the (0, ±1) diffraction orders at slightly red-shifted wavelengths, and these diffraction orders are degenerate [35,41,57]. Under TE-polarized light, SLRs follow (1, 0) and (−1, 0) diffraction orders. For superlattice SLRs, the TE modes had opposite k-vectors, corresponding to two waves propagating in opposite directions. At off-normal angles, the two k-vectors cancel to generate new modes in the dispersion diagram where the net k-vector is zero (Fig. 3e and f). At a band-edge (or at any net zero wavevector), superlattice SLRs sustain a high local density of optical states (LDOS), which opens prospects to manipulate light–matter interactions including photoluminescence (PL) modification, nanoscale lasing, nonlinear optical processes, and quantum optics [58,59].

Dispersion diagrams can also be measured with a k-space setup where the image of the back-focal plane is focused on a spectrometer slit to resolve angular energy distributions of transmitted light. Angular energy maps directly represent the in-plane momentum relation of NP arrays, and dispersion diagrams with distinct features have been recorded from arrays fabricated into square, rectangular, hexagonal, honeycomb, and Lieb lattices [60].

**Strong and weak coupling effects with organic molecules and materials**

Surface lattice resonances offer unique prospects for coupling with quantum emitters. Different from LSP resonances of single NPs, the collective lattice modes can support high-quality cavities and directional radiation [61]. The large LDOS and high intensity in the localized EM hot spots can affect the strength of light–matter interactions, resulting in two broad categories: weak or strong coupling regimes.

**Weak coupling: shaping the fluorescence emission**

Organic molecules are attractive for testing fundamental interactions with lattice resonances because of their large dipole moments, solubility in polymers and solvents, and diversity in their emission and absorption wavelengths [62]. Minor drawbacks include their limited stability under high excitation intensities. Enhancement of the fluorescent emission was observed from arrays of long Au nanorods (Fig. 1f) coated with a 50-nm polymer matrix containing ATTO 680 fluorescent molecules (0.01 mM) [63]. When the pump polarization was along the short axis of the nanorods (Fig. 4a), the fluorescence increased by sevenfold, and the enhanced emission followed the SLR...
coupled to the (1, 0) diffraction mode (Fig. 4b). Excited dye molecules preferentially decay into SLRs because the high LDOS improves light extraction. Similarly, when pump polarization was parallel to the long axis of the nanorods (Fig. 4c), the quadrupolar SLR coupled to the (0, 1) diffraction order also contributed a ten-fold enhancement in fluorescence [49]. Because quadrupolar LSPs are dark, off-normal detection was required. Fluorescence enhancement was much smaller if only photonic modes were considered (Fig. 4d).

Strong coupling with organic dye molecules
The strong coupling regime is defined as when energy exchange rates of the interacting entities are faster than loss rates [64]. Energy exchange in time results in splitting of the resonant energy in frequency into the so-called lower and upper polariton bands. The splitting, called Rabi splitting, can be visualized as an avoided crossing in the dispersion diagram, where modes of the uncoupled system intersect. Rabi splitting must be larger than the linewidths of the uncoupled modes and is directly proportional to the dipole moment of the emitter and square root of dye concentration [64].

Although strong coupling between surface plasmon polaritons and molecular excitons has been observed [64,65], interactions between SLRs and organic emitters offer opportunities to explore the effects of collective modes with long life-times. For example, strong coupling was observed between Ag NP arrays and high concentrations (200 mM) of Rhodamine 6G (R6G) [66,67], which involved three different types of excitations: lattice plasmons, LSPs, and molecular excitons. Avoided crossings between the diffraction modes and LSP resonance can be seen in the dispersion diagram (Fig. 5a, blue dots), with coupling strengths of 107 meV and 142 meV between the LSP and the first-order and second-order diffraction modes. Rabi splitting on the order of 100 meV between the R6G excitons and the LSP—as well as the LSP and the two diffraction modes—can also be observed (Fig. 5a, red dots), but direct coupling between R6G
excitons and diffraction modes was negligible. Notably, coupling between dyes and SLRs was mediated by the LSP component of the lattice modes.

Strong coupling between SLRs and molecular excitons also implies that distant emitters in the lattice can be spatially coherent. When emitters strongly couple to SLRs, the hybrid modes are expected to show properties of both constituents. Organic dyes coupled to Ag nanorod arrays were found to be spatially coherent [68], with strong coupling between excitons and the SLRs (150 meV) since the molecular absorption was below the LSP wavelength. In a double-slit set-up, interference fringes were measured in the dispersion diagram of the dye with NP arrays, which indicated spatial coherence (Fig. 5b). Evolution of spatial coherence from strong to weak coupling was achieved by decreasing the dye concentration, and coherence lengths $L$ of 6–10 $\mu$m were extracted both in weak and in strong coupling regimes. Notably, these long coherence lengths were maintained even when the hybrid mode was very exciton-like due to the existence of the SLR component in the hybrid.

**Strong and weak coupling to generate condensates**

In systems of inorganic and organic semiconductors combined with microcavities, hybrids of strongly coupled excitons and cavity modes (exciton–polaritons) have been shown to condense into a ground state that forms a macroscopic coherent quantum state [64,69,70]. Radiative recombination of exciton–polaritons can produce coherent emission similar to lasing, or called polariton lasing. Polariton lasers do not require population inversion, and hence the thresholds can be very low. Exciton–polariton condensates, including both Bose–Einstein condensates (BECs) and polariton lasing, and physical phenomena originating from non-linear interactions of exciton–polaritons are significant. In plasmonic NP arrays, strong light–matter coupling of excitons to SLRs can also produce hybrid light–matter quasiparticles [64]. The possibility of thermalization of exciton–polaritons, the redistribution of energy toward lower values and ultimately condensation [69], has been demonstrated in NP arrays [71], and polariton lasing has been observed [72]. These examples open possibilities for strongly coupled condensates, and recently, a BEC in the weak coupling regime was observed in a plasmonic NP array [73].

**Nanoscale plasmon lasing**

One of the most powerful applications of the properties of SLRs is their use as unconventional nanolasing cavities. The concept of a plasmonic nanolaser was first introduced as a spaser (surface plasmon amplified stimulated emission of radiation) [74], in which quantum emitters resonantly transferred their energy to plasmon excitations, and then the highly localized EM fields would lead to stimulated emission. Although plasmon lasing was first realized in hybrid waveguide modes—in a tour-de-force result—from semiconducting nanowires coupled to surface plasmon polaritons in supporting metal films, this architecture had some disadvantages, including high absorption loss of plasmonic films, operation at low temperatures [75,76], and special geometric designs to decrease internal losses [77].

NP arrays supporting SLRs are an ideal nanocavity for nanoscale lasing because of their ultra-narrow linewidths and sub-wavelength localized field enhancement around the NPs [21,26,28]. Despite the absence of closed cavity walls, slow light can be trapped at the SLR band-edge ($k = 0$) with a standing wave formed across the lattice because of in-phase oscillations of dipole moments from each NP (Fig. 2b and c). The array structure enables the amplified plasmons to be converted into free-space light and result in spatially coherent emission in the direction normal to the arrays [78].

**Lasing from single-lattice nanoparticle arrays**

Distributed feedback lasing has been observed by incorporating weakly coupled Au NP arrays (no SLR) in a polymer waveguide although emission was not related to the NP LSP [79]. Lattice plasmon lasing action—where the lasing signal was at the same wavelength as the SLR mode—was first reported at room temperature in 2D arrays of Au and Ag NP arrays embedded in polymer matrix filled with IR-140 organic dye [57]. When the dye was optically pumped by 800-nm fs pulses, excitons resonantly transferred their energy into the collective plasmon mode. The lasing

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**FIGURE 5**

Strong dispersion of the extinction spectra. Blue dots present the extinction maxima with the bare Ag NP array only, and red dots represent the extinction maxima when 200 mM of R6G in a 50-nm-thick PMMA layer was added on top. Blue and red solid lines are fitted with a three- and five-coupled modes models, respectively. Horizontal solid line indicates single-particle resonance, and dashed and dashed-dotted lines the R6G main absorption peak and absorption shoulder, respectively. Reproduced with permission from [68]; copyright 2014 American Physical Society.

Dispersion of the extinction spectra. Blue dots present the extinction maxima when 200 mM of R6G in a 50-nm-thick PMMA layer was added on top. Blue and red solid lines are fitted with a three- and five-coupled modes models, respectively. Horizontal solid line indicates single-particle resonance, and dashed and dashed-dotted lines the R6G main absorption peak and absorption shoulder, respectively. Reproduced with permission from [68]; copyright 2014 American Physical Society.
emission showed a critical threshold behavior (~0.23 mJ/cm²) [57]. This architecture is general, and lasing was also observed with NP arrays coated with a different dye (R6G) in polymer [80]. The thresholds of lattice plasmon lasers can be decreased by dissolving the dye gain in organic solvents (Fig. 6a and b). Not only were the molecules solubilized and more uniformly distributed but also dyes in the EM hotspots were constantly being refreshed because of Brownian motion [35]. Fig. 6c shows that the lasing signal exhibited high directionality normal to the surface with low divergence angle (<1.5°). Exploiting the refractive index tolerance of SLRs between substrate and superstrate [54] enabled dynamic control of lasing action. Real-time nanolasing tunability was achieved when Au NP arrays were integrated into a microfluidic device over the entire bandwidth of the dye (Δλ = 50 nm) when different liquid gain materials surrounded the NP arrays.

A semi-quantum mechanical simulation method treating the four-level electronic system of the dye quantum mechanically and SLR excitations by Maxwell’s equations revealed the microscopic details of lasing action [57,81]. Fig. 6d shows that when an external pump excited gain, population inversion built up between states 2 and 1, and the energy of the excitons was resonantly transferred to plasmons to result ultimately in far-field emission. Time-evolution of the population inversion was characterized by rate equations modified with the total EM fields in the system. Macropolarization of the EM fields modified absorption and emission of dyes, and the self-consistent interactions between dye emission and EM fields were modeled to simulate the lasing process. Fig. 6e indicates that below lasing threshold, the stimulated emission rate was negligible compared with the spontaneous emission rate; above threshold (Fig. 6f), however, the stimulated emission rate increased by orders of magnitude. One critical finding of this semi-quantum model was that deep-sub-wavelength regions of population inversion were co-localized with the EM hotspots—only gain in the vicinity (ca. 25 nm) of plasmonic NPs contributed to the lasing action.

**Lasing from finite nanoparticle arrays**

Finite NP arrays provide an out-coupling mechanism for dark modes into the far-field because of dipolar radiation effects at the array edges [82]. Fig. 7a shows that as the pump power increased, an intense narrow emission peak at the upper energy mode appeared first, and then a second peak at lower energy mode emerged later. The stronger lasing peak at higher energy can be attributed to the dark mode above the array diffraction lines, while the weaker lasing peak at lower energy was from the bright mode below the diffraction lines (Fig. 7b). These two modes showed distinct far-field emission patterns (Fig. 7c): the upper mode was a hybrid mode that showed radiative character of bright dipolar modes at the edges and a dark quadrupole mode in the center of the array. The lower energy mode showed radiation mainly from the center of the single patch, where the dipole moments of the NPs were maximized.

**Superlattice plasmon lasing**

Because the position of the SLR can result in plasmon lasing at the same wavelength [35,57], the ability to create multiple SLRs can result in controlled multi-mode nanolasing. Precise control over multiple lasing modes within a single device is critical for next-generation opto-electronics and can facilitate nano-scale multiplexing and optical processing [83–85]. Superlattice SLRs in hierarchical NP arrays (Fig. 8a) produce multi-modal lasing...
peaks at positions that can be understood by a detailed understanding of the contributing band-edge modes [86]. Multiple lasing peaks at $\lambda_{\text{SL}}^I$, $\lambda_{\text{SL}}^\Pi$, and $\lambda_{\text{SL}}^\Delta$ with large modal spacing ($\Delta \lambda = 10 \text{ nm}$) and ultra-narrow linewidths ($<0.5 \text{ nm}$) were observed from NP superlattices (length $l = 18 \text{ nm}$, patch periodicity $A_0 = 24 \text{ nm}$) surrounded by IR140-DMSO (Fig. 8b). Comparing transmission spectra of superlattice NPs at $\theta = 0^\circ$ with their lasing spectra, $\lambda_{\text{SL}}^I$, $\lambda_{\text{SL}}^\Pi$, and $\lambda_{\text{SL}}^\Delta$ can be correlated in a straightforward manner with the two superlattice SLRs; however, the passive mode corresponding to lasing at $\lambda_{\text{SL}}^I$ was missing. Dispersion diagrams revealed that $\lambda_{\text{SL}}^\Pi$ could be attributed to new band-edge modes at non-zero wavevectors (Fig. 8c). Hence, the lasing mode $\lambda_{\text{SL}}^I$ had origins similar to that of the single lasing mode in single-lattice NP arrays, [35,57] and $\lambda_{\text{SL}}^\Pi$ and $\lambda_{\text{SL}}^\Delta$ were lasing modes attributed to patch–patch coupling. The formation of band-edge modes at non-zero wavevectors is unique to plasmonic systems (vs. pure photonic) because of strong near-field coupling between patches. Variations in patch periodicity resulted in controlled lasing modes from different band-edge states, and changes in NP sizes could manipulate the input–output light–light behavior of the different modes.

Below lasing threshold, spontaneous emission from dye molecules surrounding the NP arrays showed a small reduction in decay lifetime because of the Purcell effect (800 ps). Above threshold, only two lasing wavelengths $\lambda_{\text{SL}}^I$, $\lambda_{\text{SL}}^\Pi$ were observed at this pump power because the multi-modal lasing was power-dependent ($\lambda_{\text{SL}}^\Delta$ was not visible under this condition) (Fig. 8d). A significant reduction of lifetime was observed at both lasing modes because of fast stimulated emission. $\lambda_{\text{SL}}^I$ showed decay lifetimes similar to that of single-lattice NP arrays (~13 ps), but $\lambda_{\text{SL}}^\Pi$ had a longer decay lifetime (~41 ps) because the patch–patch mode could trap photons for longer times. Interestingly, $\lambda_{\text{SL}}^I$ emerged earlier than $\lambda_{\text{SL}}^\Pi$ because of the overall stronger near-fields at $\lambda_{\text{SL}}^I$. These dynamics studies demonstrated that the photonic features of the superlattice SLRs allowed for longer photon lifetimes in the cavities and better optical feedback, while the plasmonic features resulted in faster population inversion build up around the NPs in the EM hotspots.

### Interactions with electronic materials

Recently, strongly coupled NP arrays have been integrated with electronic materials, including 2D transition metal dichalcogenides (TMDs) [87], carbon nanotubes (CNTs), [88] and hexagonal boron nitride (h-BN) [89]. Like their organic counterparts, inorganic materials exhibit a range of distinct properties, from modified photonic band structures to enhanced single-photon emission.

Single-layer TMD materials (2D TMDs) exhibit unique optical and electronic properties. As the dimensionality of the semiconductors is reduced, the electronic band gap changes from indirect to direct [90]. Their large exciton binding energies, which result in efficient light emission and large absorption cross-sections, offer possibilities for Wannier–Mott exciton (delocalized) coupling to SLRs. Importantly, Ag NP arrays could be fabricated by e-beam lithography on single-crystalline MoS$_2$ flakes without damage (Fig. 9a). In the dispersion diagram, the SLR was visible along with the avoided crossing of the exciton–polariton bands in the strong coupling regime [87]. Compared with the case of strong coupling with dye molecules (localized excitons) with energies on the order of 150 meV, the measured coupling strengths were 10–20 meV; however, long-range SLRs provide coupling of MoS$_2$ with plasmonic resonances beyond the length scales of individual NPs.

Semiconducting carbon nanotubes (CNTs) can emit light at wavelengths that depend on their chirality and surface ligands [91,92], but applications in optical devices have been hindered by their low PL efficiency (<0.1%) [93]. CNTs can be dried into mats of random networks so their excitons can couple to both TE and TM SLRs of Au NP arrays. A top coating layer of 150-nm poly(methylmethacrylate) for index-matching the glass substrate to preserve high-quality SLRs. In the weak coupling regime [94], CNT emission was tailored by SLRs to achieve broadband tunable emission. In the strong coupling regime [88], high concentrations of CNTs resulted in hybridization of excitons and SLRs with coupling strengths (Rabi splitting) of 120 meV (Fig. 9b).

Another electronic material that was recently coupled to SLRs is 2D hexagonal boron nitride (h-BN), whose defects can show room temperature single-photon emission. To understand how the single-photon emission changed in the presence of SLRs, defect locations within the flake were first determined by PL imaging, and then the same h-BN flake was assembled on 2D...
FIGURE 8
Multi-modal nanolasing in NP superlattices. (a) SEM image of Au superlattice arrays with NP spacing $a_0 = 600$ nm, patch side length $l = 18$ μm and patch periodicity $A_0 = 24$ μm. (b) Lasing emission profile (black curve), dye emission profile (red curve), linear optical properties (blue curve). (c) Angle-resolved emission spectra of multi-modal lasing. (d) Life time measurements of the multiple lasing modes by time-correlated single-photon counting. Reproduced with permission from [86]; copyright 2017 Nature Publishing.

FIGURE 9
Electronic materials coupled to NP arrays. (a) SEM image of monolayer MoS$_2$ below Ag NP array. (b) Angle-resolved reflectance spectra of the sample in (a). Reproduced with permission from [87]; copyright 2016 American Chemical Society. (c) Scheme of a carbon nanotube coupling with Au NP arrays. (d) Dispersion measurements showing the strong coupling of excitons in carbon nanotubes to different SLRs. Reproduced with permission from [88]; copyright 2016 American Chemical Society. (e) SEM image of hBN on top of a Ag NP array. (f) $g^{(2)}$ measurements comparing pristine hBN and hBN coupled with SLRs. Single-photon emission is preserved in the coupled system. Reproduced with permission from [89]; copyright 2017 American Chemical Society.
arrays of Ag and Au NPs. This deterministic coupling resulted in enhanced PL emission by 2–3-fold because of the Purcell effect and with a corresponding reduction in decay lifetime [89]. Second-order coherence measurements showed that even after weak coupling interactions with SLRs, the single-photon emission still preserved its quantum profile (Fig. 9c). Promisingly, this work demonstrated that large-area NP arrays provide a versatile platform for coupling to single-photon emitters without need for precise control over their location.

**Other applications of NP arrays**
The unique properties of SLRs have far-reaching applications, from surface-enhanced Raman scattering (SERS) to solid-state lighting.

**SERS and sensing**
Nanoscopic structural features on plasmonic NPs are critical to enhance SERS and other spectroscopic responses, where sharp tips and small gaps have been found to show the largest enhancements [95]. SLRs provide a different way to enhance the Raman response, where NP array spacing has been shown to affect SERS enhancements [46]. By tuning the SLR to protein absorption bands [96], detection sensitivity was increased (Fig. 10a). Systematic variation of NP size and lattice constant led to a universal scaling law of sensitivity for refractive index sensors [97], where the figure of merit depended only on spectral differences between the diffraction mode and the SLR, independent of the metal.

**Solid-state lighting**
Arrays of plasmonic NPs are already having a large impact in solid-state lighting and LED technology [5,98]. Because the emission of LED materials is isotropic, optical components are needed to control the direction of radiation; however, NP arrays added to the luminescent layer can enhance emission and improve light outcoupling [5,38,99]. Fig. 10b shows how hexagonal NP arrays integrated with LEDs can result in directional enhancement [34,38,39]. One challenge of this platform is the intrinsic absorption of the metal NPs that can reduce external quantum efficiency of LEDs [100], but a proposal to suppress resonant absorption and system losses using coherent control can potentially overcome the issue [101]. Semiconductor quantum dots have also been proposed as an alternative in solid-state lighting [102], and arrays of metal NPs have controlled emission properties of quantum dots by changing the array geometry [103–105] or adding liquid crystals [36]. By controlling the spectral overlap between the emission bandwidth of quantum dots and SLRs, the angle of enhanced emission and polarization, as well as the reduction in lifetime, can be controlled (Fig. 10c).

**Electroluminescence**
One significant step towards the integration of optical structures in devices is to drive them electrically. Fig. 10d depicts an electrically driven field-effect transistor that incorporated SLRs for enhanced emission and directionality [106]. By overcoming problems of charge mobility of organic semiconductors, the prospects of electrically driven lasers using feedback by SLRs are tantalizing.

**Conclusions and prospects**
Metal NP arrays are an exciting platform for a range of fundamental studies and technological applications. The primary characteristics of SLRs combine the desirable properties of plasmonics and photonics: high localized EM field enhancements and high-quality resonances. With advances in fabrication tools, the scalable production of NP arrays has enabled integration with a wide
range of emitters, from organic dyes to semiconducting quantum dots to 2D electronic materials, and in both weak and strong coupling regimes. This simple system offers rich properties, and the future is bright for open challenges that require a diverse materials and scientific community to solve.

First, understanding and determining the cavity mode volume, a classical concept in optics, of SLRs is non-trivial because of the debate regarding the reliability of using absorptive materials as cavities. Conventionally, the Purcell factor $F$ is defined by the ratio between quality factor $Q$ and mode volume $V$ and is used to quantify the enhancement of transition rate in emitters [107]. Although $Q$ can be extracted from the linear optical properties, $V$ cannot easily be applied to plasmonic cavities because of their divergent field profile [108,109]. The “open cavity” architecture of NP arrays further complicates this problem. Field delocalization also results in larger mode volumes that might limit studies with single molecules and isolated quantum emitters. Modeling that assesses $F$ would be helpful for a complete picture of the plasmonic effect on emitters [110,111], and experimental methods that determine internal losses would also be beneficial [100].

Second, because of the accessibility of the NP array platform, more emitters are being coupled to SLRs, and theories that include active and functional materials need to be developed. Although the coupled oscillator model can quantitatively analyze the anti-crossing behavior in the dispersion diagram and calculate coupling between SLR with absorption and emission bands of emitters [66,87], this model is merely functioning as a data-processing tool to extract the coupling strengths. More fundamental approaches describing the electronic structure of quantum emitters and hybridization with SLRs can provide better a physical picture. For example, modeling excitons with electronic band structure and considering the exciton–exciton energy transfer and dephasing at high emitter concentrations will provide more detailed understanding of plasmon–exciton coupling. Also, the amplified spontaneous emission observed in lattice plasmon lasers cannot currently be described fully because the excitation and emission are off-normal and the propagating mode is dispersive. Recently, the Liouville–von Neumann equations were used to describe plasmon–dye coupling for systems involving 1D slit arrays and show the expected Rabi splitting [112]. This new method could inspire the next experiments to test the coherence of the emitters in plasmonic cavities.

Finally, open questions and emerging applications of plasmonic NP arrays include strong light–matter coupling and condensation of exciton–polaritons to form macroscopic quantum states. For example, the role of different lattice modes and materials in exciton transport and condensation phenomena is still unclear. Also, although the decay of condensed exciton–polaritons can show coherent emission like stimulated emission in conventional lasers, their origin from the stimulated scattering of bosons is different. NP arrays offer exciting platforms to study condensates because their open cavity structure allows direct access to spatial and temporal evolution of condensation.

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