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Strong light–matter coupling and exciton-polariton condensation in lattices of plasmonic nanoparticles [Invited]

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Arrays of metallic nanoparticles support collective plasmonic resonances known as surface lattice resonances (SLRs). The strong and delocalized electromagnetic fields associated with SLRs provide an excellent platform for experiments within the realm of light–matter interaction. The planar architecture of these arrays also provides a feasible system for coupling to different materials. One of the areas where SLRs have demonstrated their potential is strong light–matter coupling, with possible applications in nonlinear optics, coherent light generation, photochemistry, and optoelectronics. In this perspective, we describe how SLRs are formed in arrays of plasmonic nanoparticles, introduce different materials used for strong coupling with SLRs, discuss some experiments that demonstrate the nonlinear emission of strongly coupled organic molecules with SLRs, and give our vision on future research directions of strongly coupled SLRs with organic molecules. © 2019 Optical Society of America

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1. INTRODUCTION

The rise of the field of plasmonics after the seminal work of Ebbesen et al. has led to a paradigm shift in our understanding of light–matter interaction at the nanoscale [1]. The ample opportunities for manipulating electromagnetic radiation using different materials, structures, and geometries have found extensive applications in different fields, such as nano-optics [2], photovoltaics [3], nonlinear optics [4], light emission [5], and single molecular detection and sensing [6,7].

Among all possible plasmonic structures, one particular system has attracted significant attention: arrays of metallic nanoparticles with particle separation comparable to the wavelength of light and supporting optical modes that propagate in the plane of the array [8,9]. These modes are known as surface lattice resonances (SLRs), and combine characteristics of resonances in single nanoparticles, such as strong field enhancement due to the plasmonic effect, with collective phenomena in arrays, like diffraction [10–16]. SLRs are the result of the enhanced radiative coupling between the individual nanoparticles within the lattice [17]. This coupling leads to the formation of hybrid plasmonic–photonic modes that contain rich physics. Compared to single plasmonic nanoparticles, in which the field enhancement usually extends up to a few nanometers from the particles, SLRs can enhance significantly the electromagnetic field at distances of several hundreds of nanometers [18,19].
to form exciton-polaritons. Exciton-polaritons are bosonic quasi-particles that can undergo Bose–Einstein condensation at sufficiently high densities. Recently, organic fluorophores have been used as the source of excitons for exciton-polariton condensation experiments. We focus here on the mechanisms leading to exciton-polariton condensation of SLRs strongly coupled to organic fluorophores and the dominant processes involved in the condensation dynamics. We finish with a future perspective on how the field of strong coupling of excitons with SLRs may evolve in the future.

2. DIFFRACTION AND RAYLEIGH ANOMALIES

In 1902, Wood observed a surprising phenomenon with an elusive origin: an increase of the intensity, followed by a sudden drop, for certain wavelengths in the spectrum of a continuous light source after passing through a metallic grating [54]. He even pointed out the important characteristic that this effect can be seen only for p-polarized light. Unable to explain the origin of this phenomenon, Wood named these intensity irregularities as “singular anomalies.” A few years later, a comprehensive explanation for these anomalies was given by Lord Rayleigh purely based on the propagating properties of the wave and the laws of refraction and reflection. Lord Rayleigh pointed out that an anomaly occurs at the wavelength for which a scattered wave emerges tangentially to the grating surface [55,56].

These efforts led to a theory that could predict the frequencies of these anomalies with partial success. However, a full agreement between the measurements and the model was never obtained. The discrepancies result from overlooking the role of surface plasmons at the surface of metals, a phenomenon that was not discovered until many years later. The model that was proposed by Lord Rayleigh cast the formalism of modern diffraction theory and it is used to predict the energy-momentum dispersion of the diffracted beams. This theory correlates the momentum of the diffracted beam \( \mathbf{k}_d \) to the momentum of the incident beam \( \mathbf{k}_i \) and the reciprocal lattice vectors of the grating \( \mathbf{G}_j \) with the law of conservation of momentum:

\[
\pm k_{i,d} = k_{i,j} + G_j. \tag{1}
\]

Throughout this paper, we refer to the singular anomalies as “Rayleigh anomalies” (RAs). These RAs correspond to the intensity increase observed by Wood and they are the in-plane orders of diffraction in the lattice, i.e., the condition at which a diffracted order becomes evanescent. The RAs can be calculated with Eq. (1). (Note that the decrease of intensity reported by Wood was due to the grating assisted coupling of the incident wave to surface plasmon polaritons in the metal.) Expanding this equation for a rectangular lattice with the pitch sizes of \( a_x \) and \( a_y \), and considering that the parallel component of the incident wave vector is along the x-direction, leads to the following dispersion relation:

\[
E(k_{iy})^2 = \left( \frac{\hbar c}{n} \right)^2 + \frac{k_{iy}^2}{a_y^2} + \frac{2\pi}{a_y q} + \frac{2\pi}{a_x p},
\]

where \( p, q \) are integers giving the orders of the RAs in the lattice, and \( n \) is the effective refractive index of the medium where the grating is embedded. We frequently use the modes formed by \((1, 0), (-1, 0), \) and \((0, \pm 1)\) orders. The first two modes have a linear dispersion, while the \((0, \pm 1)\) modes are degenerate and have a parabolic dispersion.

3. SURFACE LATTICE RESONANCES

Isolated metallic nanoparticles, or what has been coined as the term “optical antennas” [57], are nanometer-scale particles that manifest plasmonic resonances [or localized surface plasmon resonances (LSPRs)] in the visible and infrared part of the electromagnetic spectrum. These resonances are coherent oscillations of the free electrons driven by an external electromagnetic field. The high intrinsic polarizability of these optical antennas, due to the LSPRs, leads to efficient scattering and absorption at resonant frequencies [58]. The enhanced electromagnetic field intensity at close proximity to these nanoparticles is a direct consequence of this large scattering cross section, leading to a strong radiative decay channel for LSPRs. Additionally, due to the enhanced absorption efficiency, the Ohmic dissipation of electromagnetic energy in these nanoparticles is considerable—an undesirable effect that possesses important challenges for the application of plasmonic nanoparticles in different disciplines [59].

Improving the quality of plasmonic resonances, such as their lifetime and quality factor, has led to the use of arrays of nanostructures, where LSPRs supported by individual nanoparticles interact with the in-plane orders of diffraction or RAs supported by the array. The improvement of the quality factor relies on the enhanced radiative coupling of the individual nanoparticles, and as mentioned before, the modes that are formed through this condition are the SLRs. Arrays of optical antennas supporting SLRs can be regarded and the optical analog of antenna phased arrays that emit electromagnetic waves only in defined directions given by the relative phases of the individual antennas [60,61]. Some examples of such arrays are shown in the scanning electron microscope (SEM) images of Figs. 1(a)–1(c). This beaming enhances the emission in these directions, while reducing the radiative losses in other directions by interference, with a net reduction of the total radiation losses.

A numerical method to calculate the spectral properties of SLRs is the coupled dipole approximation [12,13,15]. In this approach, the nanoparticles are approximated as point dipoles. An array of \( N \) nanoparticles is considered, such that the polarizability and the position of each nanoparticle in the array is \( \alpha_i \) and \( r_i \), respectively. The polarization at each particle within the lattice is given by the relation \( P_i = \alpha_i E_{\text{loc},i} \), where \( E_{\text{loc},i} \) represents the local electric field at the position of \( r_i \). The local electric field at particle \( i \) is the sum of the incident field \( E_{\text{inc},i} \) and the retarded fields \( E_{\text{dipole},i} \) arising from the rest of the \( (N-1) \) dipoles within the array, and it can be self-consistently calculated with the equation

\[
E_{\text{loc},i} = E_{\text{inc},i} + E_{\text{dipole},i}
\]

\[
= E_0 \exp(ik \cdot r_i) - \sum_{i=1, i \neq j}^N A_{ij} \cdot P_j, \quad (i = 1, 2, \ldots, N),
\]

\[
\tag{3}
\]
The extinction cross section can be found by assuming that the induced polarization on each particle is the same. By solving this equation, the following relation for the effective polarizability ($\alpha^\ast$) is obtained by:

$$\alpha^\ast = \frac{1}{1/\alpha - S},$$

where $S$ represents the retarded dipole sum that takes into account the particles separation and the configuration of the lattice, and it is given by

$$S = \sum_{j \neq i} \left[ \frac{(1 - ik \cdot r_{ij})(3 \cos^2 \theta_{ij} - 1) \exp(ik \cdot r_{ij})}{r_{ij}^3} + \frac{k^2 \sin^2 \theta_{ij} \exp(ik \cdot r_{ij})}{r_{ij}} \right],$$

where $\theta_{ij}$ is the angle between $r_{ij}$ and the direction of the polarization. After obtaining $\alpha^\ast$, the absorption ($C_{abs}$) and scattering ($C_{scat}$) cross sections can be calculated with

$$C_{abs} = 4\pi k^3\alpha^\ast$$

and

$$C_{scat} = \frac{8}{3} \pi k^4 |\alpha^\ast|^2,$$

from which the extinction cross section can be obtained:

$$C_{ext} = C_{abs} + C_{scat}.$$

An example of extinction spectra for a single nanoparticle and a lattice of nanoparticles is displayed in Fig. 2(a). In the couple dipole model, when the difference between the imaginary components of $1/\alpha$ and $S$ is small and the real parts are equal, the denominator in Eq. (5) approaches zero, and the extinction cross section is maximum. This is the condition which

![Fig. 1. SEM images of samples with (a) square symmetry made of aluminum nanoparticles with pitch size of 400 nm (Ref. [21], reproduced with permission from APS), (b) hexagonal symmetry made of aluminum nanoparticles with pitch size of 475 (Ref. [62], reproduced with permission from APS), and (c) rectangular symmetry made of silver nanoparticles with pitch sizes of 380 and 200 nm (Ref. [63], reproduced with permission from OSA).](image)

![Fig. 2. (a) Calculated spectra of the extinction cross sections of a single particle (green) and a lattice of particles with pitch of 480 nm using the coupled dipole approximation. The particles are considered as Ag ellipsoids with semi-axes $a = 30$ nm and $b = c = 120$ nm, embedded in a homogeneous medium with a refractive index of 1.515. (b) Real and imaginary parts of $S$ and $1/\alpha$. The SLRs correspond to the energy at which $\Re(1/\alpha)$ equals $\Im(S)$ and the difference between the imaginary components of $S$ and $1/\alpha$ is small (reproduced from Ref. [64] with permission from APS).](image)
corresponds to the excitation of SLRs and it is indicated by the dotted vertical lines in Figs. 2(a) and 2(b), where in (b) the real and imaginary parts of S and 1/Ω are shown as a function of the energy. The coupled dipole model can be used to calculate the extinction cross section of small particles that can be approximated by a point dipole. In the case where the particles are larger, such that retardation effects become important, or multipolar resonances can be excited within the frequency range of interest, other methods need to be used.

One of these methods that can capture the collective nature of SLRs is the coupled harmonic oscillators model [65,66]. Within this model, one oscillator represents LSPRs supported by individual nanoparticles and two other oscillators describe the RAs [e.g., the (1, 0) and (−1, 0) diffraction orders]. In the matrix representation, the equation of motion for the coupled systems is

\[
\begin{pmatrix}
\omega_1^2 - \omega^2 - i\gamma_1\omega \\
\omega_2^2 - \omega^2 - i\gamma_2\omega \\
\omega_3^2 - \omega^2 - i\gamma_3\omega
\end{pmatrix}
\begin{pmatrix}
x_1 \\
x_2 \\
x_3
\end{pmatrix}
= \begin{pmatrix}
\frac{\mu_0 F}{m} e^{-i\omega t} \\
0 \\
0
\end{pmatrix}.
\]

(10)

In this model, the system of three coupled oscillators with the individual resonant frequencies of \(\omega_{1,2,3}\) is driven by a harmonic field of frequency \(\omega\), acting on the first oscillator (LSPRs). The losses associated with each oscillator are represented by \(\gamma_{1,2,3}\). The coupling rates between oscillators are given by \(\Omega_{12}, \Omega_{13}, \Omega_{23}\). The mass of the first oscillator is \(m\), and \(F\) quantifies the strength of the driving field. Hence the ratio \(\frac{\mu_0 F}{m}\) represents the amplitude of the driving field. The spectra representing the optical extinction from a particle array can be calculated by taking into account the dissipated power in the first oscillator integrated over one cycle of the driving field through the relation \(\frac{3}{2} \text{Re}(F_{\text{ext}})\). It should be noted that the amplitude of the driving field does not have any particular relevance for these calculations as we are interested in obtaining the spectra for qualitative comparison. The dispersion of the RAs is introduced through the relation between the \(\omega_{2,3}\) and \(k_{||}\) that is obtained with Eq. (2).

SLRs can be considered as hybrid plasmonic–photonic modes that simultaneously manifest large spatial extension and strong electromagnetic field enhancement. This hybridization can be seen in the calculated dispersions of the SLRs using the coupled oscillator model in Figs. 3(a) and 3(b) at the anticrossing points between the flat dispersion of LSPRs at \(E = 2.6\) eV and the dispersive RAs. Close to the points where the anticrossing occurs \([k_\parallel \approx 4\text{ mrad/nm in Fig. 3(a)}\) and \(k_\parallel \approx 11\text{ mrad/nm in Fig. 3(b)}\)], the width of the resonances gets broader, indicating higher radiative and Ohmic damping due to a stronger plasmonic character. By increasing the detuning between the LSPRs and the RAs, the photonic character of the SLRs becomes more dominant, leading to narrower linewidths.

The other salient feature about SLRs is their asymmetric line shape [Figs. 3(c) and 3(d)]. This shape is known as Fano line shape and is explained through the spectral interference of modes with different linewidths. In the case of SLRs, LSPRs manifest a broad linewidth due to the strong radiative decay, and RAs are modes with a very narrow linewidth that occur only at specific wavelengths. Due to the spectral overlap and coupling of these modes, Fano resonances are formed. The Fano line shape, associated with the spectrum of SLRs, complicates the determination of the resonance quality factor and lifetime. This complication arises from the Fano parameter, which, besides the losses, it also contributes to the width of the resonance [67].

Methods used extensively to calculate the spectral response and the electromagnetic field distribution of arrays of nanoparticles beyond the dipolar approximation are numerical simulations in the frequency or time domains. We illustrate this with an example that shows the collective behavior of SLRs: the strength of SLRs depends on the number of particles in the lattice. To elucidate this effect further, we have simulated the extinction spectra and electromagnetic field distribution of finite and infinite arrays of silver nanoparticles using the finite-difference time-domain technique (FDTD Lumerical). A plane wave with the polarization along the horizontal axis is incident along the normal direction to drive the system. The extinction spectra of lattices of nanoparticles with different number of particles, together with the electric field distribution around the central particle of the lattice, are shown in Fig. 4. The lattice constant is 400 nm and the particles are 50 nm high and 50 nm wide in diameter. The lattice is assumed to be on
quartz ($n = 1.45$) and to be covered with a 200 nm layer of polymethylmethacrylate (PMMA). Placing the particles in the lattice and increasing their number leads to a gradual modification of the extinction spectrum. This modification is the result of the radiative coupling between the nanoparticles due to diffraction in the plane of the array. It should be noted that for relatively small particles (radius < 25 nm), the geometrical parameters become less relevant and the dipole approximation could be employed to describe the radiation pattern of the nanoparticles [15,68]. In this gradual modification of the spectra and the electric field with the number of particles, the formation of the long-range interactions between the particles is visible in Fig. 4(c), while for lower particle numbers the formation of the long-range interactions between the particles is less significant. Eventually, in the limit of infinite array of nanoparticles, a very large interparticle radiative coupling, along with a very narrow resonance in the extinction spectra, can be seen in Fig. 4(d). These characteristics correspond to the collective behavior of LSPRs upon excitation of SLRs.

The improved optical properties of SLRs have provided an interesting platform for many experimental and theoretical investigations of light–matter interactions. Especially interesting is the regime known as strong coupling, when the strength of the interactions exceeds the losses of the system. In what follows, we give a concise description of the concept of strong light–matter coupling and an outlook on the existing literature concerning strong coupling with SLRs.

4. STRONG LIGHT–MATTER COUPLING

If the strength of interactions between a two-level or multilevel system with an optical field of a cavity is stronger than the total losses of the system, hybrid quasi-particles known as exciton-polaritons can be formed. These quasi-particles simultaneously manifest properties of their constituent (quasi-)particles, i.e., photons and excitons. The formation of exciton-polaritons opens up an exciting avenue in the field of photonics for developing new devices with improved functionalities.

A close look into the fundamental properties of photons and excitons reveals important intrinsic limitations associated with each of them that could be potentially improved using the physics of strong light–matter coupling: unlike electrons, photons cannot interact with each other due to the lack of electric charge. The absence of mutual interactions between photons has imposed serious challenges in the fabrication of nonlinear devices operating on few-photon levels. The interacting nature of the excitonic component of exciton-polaritons can address this problem and can have an important impact on the field of optoelectronics and integrated photonics [69]. Electrons and holes in excitons can be harvested in photovoltaic applications. However, excitons are known to be susceptible to structural imperfections and disorder, leading to the localization of exciton wave functions and limiting their diffusion length and mobility. The hybrid nature of exciton-polaritons leads to spatially extended wave functions (photonic character) that result in interesting properties, such as robustness toward structural disorder and enhanced diffusion [70–75]. Hence, investigating different aspects of exciton-polariton physics is a major driving force for developing devices with improved functionalities, spanning from nonlinear optics to photovoltaics. Moreover, the possibility of altering the energy levels and surfaces in matter due to the formation of exciton-polaritons has opened up a wide perspective for controlling photochemical reactions [76–82], energy transfer [83–86], and intersystem crossing [87,88], highlighting the potential of strong light–matter interaction in different disciplines.

Within the context of quantum electrodynamics, where both matter and radiation are quantized, the problem of interaction between emitters and resonant structures, such as cavities, is described by the Jaynes–Cummings Hamiltonian. This Hamiltonian considers a single two-level system interacting strongly with the quantized electric field of a cavity [Figs. 5(a) and 5(b)]. The Jaynes–Cummings Hamiltonian is expressed as [82,90]

\[
H = \frac{1}{2} \hbar \omega_0 \hat{\sigma}_z + \hbar \omega (\hat{a}^\dagger \hat{a}) - i \frac{\hbar \Omega}{2} (\hat{a} \hat{\sigma}_+ + \hat{a}^\dagger \hat{\sigma}_-),
\]

\[
\Omega = \frac{2d}{\hbar} \sqrt{\varepsilon_0},
\]

\[
\varepsilon_0 = \sqrt{\frac{\hbar \omega}{2 \epsilon_0 V}},
\]

where $\hat{a}^\dagger (\hat{a})$ is the bosonic ladder operator responsible of creating (annihilating) a photon of energy $\hbar \omega$ in the cavity, and...
\[ \hat{\sigma}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \hat{\sigma}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \]

are the Fermionic ladder operators that express the transitions between the ground and excited states; \( \omega_0 \) is the angular frequency of the resonant transition in the two-level system and \( \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \) is the Pauli matrix denoting the energies of the states. \( \Omega \) is the Rabi frequency that quantifies the rate of energy exchange between the two-level system and the cavity photon and defines the strength of the coupling; \( d \) in Eq. (12) is the transition dipole moment associated with the two-level system, and \( \xi_0 \) is the electric field amplitude per photon in the mode volume \( V \).

The solutions of the Jaynes–Cummings Hamiltonian are coherent superpositions of the electronic excitation in the two-level system and the photon in the cavity:

\[
\Psi_{\text{LP}} = a_{\text{LP}} |g\rangle |1\rangle + \beta_{\text{LP}} |e\rangle |0\rangle, \\
\Psi_{\text{UP}} = a_{\text{UP}} |g\rangle |1\rangle + \beta_{\text{UP}} |e\rangle |0\rangle.
\]

These new hybrid states known as upper (\( \Psi_{\text{UP}} \)) and lower (\( \Psi_{\text{LP}} \)) polaritons, are the linear superposition of the product of an atom in the ground state (\( |g\rangle \)) with one photon in the cavity (\( |1\rangle \)), and the product of an atom in the excited state (\( |e\rangle \)) and no photon in the cavity (\( |0\rangle \)). The mixing terms \( a_{\text{LP}}, \beta_{\text{LP}}, a_{\text{UP}}, \beta_{\text{UP}} \) are known as the Hopfield coefficients [91].

Despite the importance of the Jaynes–Cummings model, its implications are limited to a single emitter in a cavity. In the case of interaction between many excitons and optical cavities that concerns most of the work in this thesis, the collective nature of the interactions and the presence of many two-level systems within the cavity needs to be taken into account. The extension of the Jaynes–Cummings Hamiltonian to \( N \) two-level systems interacting with a cavity mode is known as the Tavis–Cummings Hamiltonian. The eigenstates in the single excitation subspace are linear superpositions of all uncoupled states such that either a single photon is in the cavity and all the emitters are in their ground states or a single emitter is in the excited state and all the other emitters are in the ground state and no photon is present in the cavity. In this condition, the eigenstates of the system are

\[
\Psi_K = \sum_{i=1}^{N} \beta_i |g_i g_2 \cdots e_i e_N \rangle + a^K |g g_2 \cdots g_N \rangle,
\]

where \( K \) refers to the \( N + 1 \) eigenstates in this system. These eigenstates include an upper and a lower polariton, formed by the superposition of a molecular state \( |B\rangle = \frac{1}{\sqrt{N}} \sum |g_1 g_2 \cdots e_i e_N \rangle |0\rangle \) with the single photon state \( |g_1 g_2 \cdots g_N \rangle |1\rangle \). This state is known as bright state as it is coupled to the photon. Additionally, all the other \( N - 1 \) superpositions of molecular excitations are not coupled to the photon and form the dark states \( (a^K = 0) \) that cannot be detected in the spectrum [82]. In this case, the energy gap between the upper and lower polaritons states is given by

\[
G = \frac{\hbar \Omega}{2} = \sqrt{N} d \xi_0,
\]

where \( \Omega \) is the Rabi frequency. The importance of this equation is the presence of the \( \sqrt{N} \) term that scales the strength of the interaction with the square root number of two-level systems. This scaling relation underpins the majority of the experiments on strong light–matter interaction, where a very large number of quantum emitters is required to form exciton-polaritons. Recently, Chikkaraddy et al. have experimentally demonstrated the dependency of the Rabi splitting on \( \sqrt{N} \) down to the level of single molecules using gold nanospheres on a gold film [92].

Different experimental methods can be employed to investigate the strength of light–matter coupling. The most straightforward approach is to measure the dispersion of the modes supported by the system. Measurement techniques, such as angle-resolved transmission or reflection, provide such information [Fig. 5(c)]. One signature of the strong coupling regime, i.e., a regime where the strength of the interactions exceeds the total decoherence and losses of the system, is the appearance of the avoided crossing at the energies and momenta where the two modes approach each other. This avoided crossing is the result of the formation of upper and lower exciton-polaritons with an associated Rabi splitting of \( \hbar \Omega \) between the polaritons [see Fig. 5(d)]. In a classical picture, this interaction between the two modes can be expressed by a two-state Hamiltonian:

\[
H = \begin{pmatrix} E_e - i \gamma_e & G \\ G & E_g - i \gamma_g \end{pmatrix},
\]

where \( E_e \) and \( E_g \) describe the energies of the optical mode and exciton with the associated losses of \( \gamma_e \) and \( \gamma_g \), respectively. In this Hamiltonian, \( G \) describes the strength of the interaction as in Eq. (16). Note that the dispersive nature of the cavity mode can be easily incorporated into this Hamiltonian through its dependency on the detuning parameter such as momentum. Diagonalizing this Hamiltonian leads to its eigenenergies,

---

Fig. 5. Fabry–Perot cavity in the (a) absence and (b) presence of a two-level system. (c) Generic representation of the anticrossing and formation of the upper polariton (up) and lower polariton (lp) bands, with splitting \( \hbar \Omega \). (d) Energy levels of the lower and upper polariton bands for a fixed wave vector after hybridization between the cavity photons (c) and excitons (x). Figure adapted from Ref. [89] with permission from Nature Publishing Group.
which describe the energies of the upper and lower polaritons. This equation shows how the energies of new eigenstates deviate from the uncoupled ones. An example of strong coupling between a SLR and a cyanine J-aggregate is shown in Fig. 6(b).

Figure 6(a) displays the absorption spectrum of the bare J-aggregate layer.

5. STRONG COUPLING OF SLRs WITH MATERIAL EXCITATIONS

Arrays of plasmonic nanoparticles supporting SLRs have been employed by different groups to achieve strong light–matter coupling and formation of plasmon-exciton-polaritons (PEPs). The ease of fabrication, due to the planar architecture of 2D lattices, in addition to the possibility of supporting optical modes with different dispersive properties, have been the two main motivations for the use of SLRs instead of the canonical microcavities formed by two parallel mirrors. The other implicit but interesting feature of these resonances is the transparency of the lattice for most of the frequencies, except for the frequency of the SLRs. The term “open cavity” has been often used to describe this property, which lifts the restricted conditions that are imposed by other optical cavities, allowing wide access to the majority of the frequencies for pumping and probing the system. Figure 7 shows schematically the structure of a Fabry–Perot cavity and an array of plasmonic particles and their associated transmission spectra, illustrating the concept of open cavity.

Several classes of materials with different properties have been used for strong coupling of excitons with SLRs. In what follows we give a short overview of some of these studies. We also illustrate in Fig. 8 these different systems.

In addition to organic and room-temperature systems, inorganic semiconductors, such as GaAs quantum wells, have been used for strong coupling with SLRs [97]. Figures 8(a) and 8(e) show the structure of a GaAs quantum well and its associated absorbance spectra. The main motivation of this work has been the spectral shift of the exciton resonance along with the increase of the radiative decay of excitons. Excitons in GaAs quantum wells are stable at cryogenic temperatures and, due to the spin–orbit coupling, they manifest two transitions in the absorption spectrum associated with the heavy-holes and light-holes. Moreover, due to the low-temperature nature of these excitons, the thermal contribution to the inhomogeneous broadening is suppressed. The photostability of GaAs and other inorganic systems is much better compared to their organics counterparts. The reported values of the Rabi splitting (40–50 meV) are smaller than those of the room-temperature materials, due to the weaker transition dipole moment [see Fig. 8(i)].

Carbon nanotubes are another class of materials used for hybridization with SLRs [94,98]. Apart from the strong binding energy of the excitons and small Stokes shift in carbon nanotubes, their remarkable charge transport properties have made them an interesting candidate for realizing electrically driven polariton devices at room temperature. The schematic representation of a carbon nanotube and their absorbance spectrum are shown in Figs. 8(b) and 8(f). Similar to organic fluorophores, carbon nanotubes also are embedded in a polymer matrix and spin-coated on the sample. In addition to interesting electrical properties, the energy of the excitons is relatively low compared to organic fluorophores, allowing the access to lower ranges of the energy spectrum. The reported Rabi splitting energy for carbon nanotubes coupled to SLRs is around 120 meV [see Fig. 8(j)].
Organic fluorophores have been widely employed for studying strong coupling with SLRs [32, 50, 51–53, 63, 99–101]. Various families of organic fluorophores, such as rhodamine [see Figs. 8(c) and 8(g) for the structure and absorbance spectrum], perylene, and cyanine (J-aggregate form), have been used in different experiments. Generally, most of these molecules are embedded in an inert polymer matrix, such as PMMA or polystyrene, and their solution is spin-coated on the array. Frenkel excitons, generated via electronic transitions of the molecules, provide a versatile and interesting platform for studying some of the properties of collective strong coupling at room temperature due to their strong oscillator strength. Absorption and emission of organic fluorophores cover the entire range of visible and near-IR frequencies, making them flexible materials for developing emitting devices based on exciton-polaritons. However, organic compounds are susceptible to photodegradation and their photostability is not particularly high. Typical Rabi splittings associated with organic fluorophores are between 100 and 300 meV [see Fig. 8(k)].

The recent interest on transition metal dichalcogenide semiconductors (TMDs) for their pronounced different properties when they are thinned to an atomic monolayer, has led to the observation of several interesting phenomena [102]. The structure and absorbance spectrum of a WS$_2$, as one of the widely used 2D-TMDs, is shown in Figs. 8(d) and 8(h). One particular property of these materials is their high exciton binding energies in the visible due to the 2D confinement, which makes them particularly interesting for strong light–matter coupling. In this context, strong light–matter coupling of TMDs with SLRs has been reported [96, 103, 104, 105]. The absorption/emission energy and their quantum efficiency can be modified, and the strength of the coupling can be controlled by the number of the layers coupled to the SLRs [96].

6. CONDENSATION OF EXCITON-POLARITONS

As mentioned earlier, exciton-polaritons manifest properties that make them suitable platforms for nonlinear optical devices at a microscale/nanoscale. Within this paradigm, exciton-polaritons have been the subject of intensive studies in condensed matter physics with the initial motivation of achieving a source of coherent radiation similar to lasers, but without the need of population inversion. This motivation originally stems from the proposal of Imamoglu et al. in 1996, where
the bosonic nature of these quasi-particles was proposed for such a device [106]. This proposal was based on the possibility of a Bose–Einstein condensation (BEC) phase transition of exciton-polaritons at high temperatures. BEC is a state of matter, which was originally predicted by Satyendra N. Bose and Albert Einstein in 1924 [107]. In BEC, a significant number of bosons, e.g., gases of dilute atoms, molecules, quasi-particles or photons, occupy the lowest quantum state. This ground-state occupation forms a macroscopic coherent state that can be described with a common wave function. For uniform gas of free, noninteracting bosons, the critical temperature for achieving BEC is given by [108]

$$T_c = \frac{3.3 \hbar^2 n^{2/3}}{mk_B},$$

(19)

where $n$ and $m$ are the number and the (effective) mass of the bosons and $k_B$ is the Boltzmann constant. Despite the fact that dilute atomic gases such as sodium and rubidium have been used for the pioneering experiments demonstrating BEC, they require temperatures as low as 100 nK, posing significant experimental challenges for implementing these experiments [109,110]. One approach to manifest BEC at higher temperatures is to use (quasi-)particles with lower (effective) masses. Due to the photonic character of exciton-polaritons, their effective mass can be 4 to 5 orders of magnitude smaller than the mass of an electron, pushing the limits of BEC to room temperature.

Taking into account the nature of BEC, a significant difference between conventional lasers and exciton-polariton condensates (alternatively called exciton-polariton laser) is the thermodynamic state of the system. To create lasing action, one needs to drive the system out of equilibrium to create population inversion. The dynamics of exciton-polariton BEC is governed by the tendency of the system for reaching thermodynamic equilibrium via various thermalization processes [91]. However, due to the intrinsic losses of the cavity and the excitons, exciton-polariton condensates cannot reach thermodynamic equilibrium and they form nonequilibrium condensates in driven-dissipative systems. As a result of this fundamental distinction, thresholds for creating coherent light emission are predicted to be lower for exciton-polariton condensates than for conventional photon lasers based on population inversion in a gain medium [106]. As an example, the minimal critical pump to achieve lasing as a function of coupling strength is calculated for an organic-based exciton-polariton laser as a function of the coupling strength ($G\sqrt{N}$) and the crossover from weak to strong coupling. Note that the coupling strength scales with the number of the molecules ($\sqrt{N}$). Reproduced from Ref. [111] with permission from APS.

Fig. 9. Minimal critical pump fluence (lasing threshold) calculated for an organic-based exciton-polariton laser as a function of the coupling strength ($G\sqrt{N}$) and the crossover from weak to strong coupling. Note that the coupling strength scales with the number of the molecules ($\sqrt{N}$). Reproduced from Ref. [111] with permission from APS.

The thermalization of exciton-polaritons strongly depend on the choice of materials and the circumstances in which the experiments are done. The canonical systems for condensation experiments are Fabry–Perot cavities with inorganic semiconductors, such as InGaAs quantum wells embedded in GaAs. As pointed out, Wannier–Mott excitons in inorganic quantum wells have extended wave functions over many unit-cells of the semiconductor crystal, capable of showing strong dipole–dipole interactions. This characteristic makes the mutual dipolar interactions between exciton-polaritons and also their interactions with the exciton-polariton reservoir as the main relaxation mechanism in thermalization processes toward condensation [see Fig. 10(a)] [91]. However, their exciton binding energy is usually lower than the thermal energy of room temperature, $k_B T$, where $T$ is the temperature, making them unstable. As a result, most of the experiments need to be done at cryogenic temperatures.

In the past few years, the use of organic compounds as active materials for providing excitons through electronic transitions has attracted a lot of interest. This interest is mainly due to the stable molecular excitons (Frankel excitons) with large binding energies that has led to the observation of exciton-polariton lasing at room temperature [63,117,118–120]. Due to the spatially confined wave function of Frenkel excitons, Coulomb interactions between these excitons are negligible despite the strong transition dipole moment associated with them. Additionally, due to strong coupling between electronic transition and nuclear configurations, vibrational dressing and excitation of the vibrational degrees of freedom in molecules is inevitable [111].

Exciton-polariton condensation at room temperature using organic molecules has been a novel approach to make low-threshold coherent light sources. However, the different properties of exciton-polaritons formed in organic systems poses new and important questions regarding the thermalization dynamics of this category of condensates. The first important difference between organic and inorganic exciton-polaritons
is the incoherent pumping scheme. Inorganic systems are usually driven by CW lasers that effectively leads to the conditions of the driven-dissipative regime, where the excitation laser continuously pumps the exciton-polariton reservoir while photons decay from the condensate due to the finite lifetime of the cavity mirrors. Moreover, lifetimes of Fabry–Perot cavities for inorganic systems are very long compared to their thermalization dynamics. These conditions lead to the formation of condensates that are close to their thermodynamic equilibrium. In contrast, organic condensates rely on the excitation with ultra-short laser pulses to reach sufficiently high density of exciton-polaritons for bosonic stimulation, i.e., a nonlinear process in which bosons are inelastically scattered into the state that has the highest bosonic population. This excitation results in an impulsive drive of the system. Moreover, the lifetimes of the cavities are very close to the time scales of the thermalization process in organic molecules, leading to highly nonequilibrium conditions.

As a result of all the differences mentioned above, understanding the physics of organic-based exciton-polariton lasing requires a thorough investigation within a new range of boundaries that are not necessarily in agreement with the behavior expected from inorganic systems.

7. THERMALIZATION OF ORGANIC EXCITON-POLARITONS AT ROOM TEMPERATURE

The thermalization mechanisms leading to condensation in organic systems are different than the mutual interactions between inorganic exciton-polaritons [Fig. 10(b)] [121]. It has been suggested that ground-state molecular vibrations play an important role in the relaxation of exciton-polaritons in organic systems. In [122], it was considered that the scattering process is mediated by a molecular photoemission with the creation of a vibrational quantum in the ground state of the molecule, assuming that the vibrational state is localized onto single molecules (Fig. 11). The immediate consequence of this model is that the energy of the condensate is defined by the vibronic replica in the molecules rather than energy of the cavity, as represented in Fig. 10(b). This is a fundamental difference with respect to inorganic systems, where the energy is defined by the exciton-polariton dispersion [Fig. 10(a)]. The model proposed in [122] is based on the kinetic equations for polariton and exciton populations with decay rates accounting for vibrationally assisted processes. Recently, in an alternative approach, a microscopic model based on the nonequilibrium Dicke–Holstein Hamiltonian has been employed, which takes into account the coupling of the vibrational degree of freedom to the electronic states of many molecules coupled to a single cavity mode [111]. This model captures phenomena such as the role of vibrational sidebands on feeding the polariton condensate, and the modification of the lasing threshold as a function of the coupling strength (see Fig. 9).

The first experimental demonstration pointing toward the effect of molecular vibrations on the condensation of organic exciton-polaritons was done by Kéna-Cohen and Forrest using anthracene micocavities [117]. One year later, it was demonstrated by Cole et al. (using J-aggregate microcavities) that the photoluminescence along the exciton-polariton band was enhanced at the energies that correspond to the Raman transitions of the molecules [123]. Note that the zero phonon line is considered to be at the exciton-polariton reservoir energy. Moreover, one needs to take into account that due to the finite linewidth of the modes at room temperature, the precise energies associated with these molecular and polaritonic modes are not well-defined. However, phenomenological models can be used to estimate the energy at which exciton-polaritons scatter into and form the condensate. Following the work of Kéna-Cohen in 2010, organic-based exciton-polariton lasing has been demonstrated using different organic compounds, such as conjugated polymers (MeLPPP) [118], TADF (2,7-bis[9,9-di(4-methylphenyl)-fluoren-2-yl]-9,9-di(4-methylphenyl) fluorene) [119], perylene molecules [63], and even proteins [120]. A common feature of these experiments is the presence of high-frequency vibrational modes coupled to the electronic transition and providing an efficient relaxation channel for condensation.

Fig. 10. (a) Polariton-polariton interactions as one of the dominant relaxation mechanisms for BEC of exciton-polaritons in inorganic systems. (b) Relaxation of exciton-polaritons via ground-state vibrational quanta to form BEC in organic systems. Note that the energy of the condensate is independent of the exciton-polariton dispersion and is determined by the energy of the vibrational quanta in the molecules ($\Delta E_vib$).

Fig. 11. Phenomenological model used by Mazza et al. to describe the process of vibrationally assisted radiative emission responsible for the efficient relaxation of the polaritons to lower energy levels. Reproduced from Ref. [122] with permission from APS.
8. PLASMON-EXCITON-POLARITON CONDENSATION WITH SLRs

Recently, it has been shown that SLRs can be used as optical modes for the formation of PEP condensates [63] (condensates of plasmon-exciton-polaritons) and photon condensates [124]. The relevance of plasmonic arrays supporting SLRs as an alternative platform for organic-based condensation experiments is on its open cavity structure, which allows broadband and easy access to the condensates for excitation and spectroscopy.

An array of silver nanoparticles strongly coupled to perylene dye was used for the first demonstration of PEP condensation [63]. In this study, the relation between strong coupling and the nonlinear behavior of the system was investigated [Fig. 12(a)]. It was shown that at low molecular concentrations ($c < 15$ wt%), where the coupling is not strong enough, only a linear emission was observed. However, a transition from linear to nonlinear emission and reduction of the emission line-width was observed by increasing the molecular concentration and enhancing the coupling strength ($c > 25$ wt%) [see Figs. 12(a) and 12(b)]. A remarkable observation was the reduction of the condensation threshold as the molecular concentration was increased, despite the strong reduction of the emission quantum efficiency of the molecules by concentration quenching [Fig. 12(c)]. It should be noted that a reduction of the quantum efficiency in normal lasers (stimulated emission) should increase the lasing threshold. However, in the strong coupling regime the quantum efficiency does not play a critical role. Other properties of this system above the threshold, such as the spectral shape and angle-resolved emission, were investigated in [63] [see also Fig. 12(b)]. Also, the spatial coherence properties of the PEPs above the threshold and the degree of the first-order coherence were quantified in [33]. In the same study, the time-resolved emission of the PEPs was investigated using a streak camera and revealing interesting features. One of these features is the time-dependent spectral red-shifting due to the reduction of PEP density in the condensate. It was also observed that the intensity of the emission is maximum at times long after photoexcitation (8 ps) highlighting the complex dynamics of PEP condensation in organic systems.

It must be noted that conventional photon lasing from the arrays of plasmonic nanoparticles supporting SLRs in the vicinity of a dye-doped layer has been reported [40,41]. Despite many similarities between photon lasing and PEP lasing, the energies at which the lasing occurs are assigned differently. In photon lasing, the energy is dictated by the energy of the optical mode and its overlap with the gain medium. However,

Fig. 12. (a) Emission intensity of perylene molecules at different concentrations coupled to an array of Ag nanoparticles as a function of the pump fluence. Up to 15 wt. % molecular concentration, the sample is in the weak coupling regime and a linear emission is observed. Increase of the concentration leads to the formation of PEPs and the nonlinear emission threshold (reproduced from Ref. [63] with permission from OSA). (b) Emission spectra for different pump fluences below and above the condensation threshold (reproduced from Ref. [63] with permission from OSA). (c) Quantum efficiency of the layer containing the molecules as a function of the molecular concentration. (d) Spatial coherence of the sample measured with a Mach–Zehnder interferometer (reproduced from Ref. [33] with permission from ACS). (e) Time-resolved emission of the sample at the energy of the PEP condensate (reproduced from Ref. [33] with permission from ACS).
PEP lasing relies on the vibrational modes of the organic molecules and the energy is independent of the SLR energy [125].

9. PLASMON-EXCITON-POLARITONS LASING/CONDENSATION IN THE PRESENCE OF DISORDER

The quality of the fabricated sample and the density of the structural imperfections and disorder in the nanoparticle array can impact the behavior of the system. Within this context, PEP condensation is not an exception either, as discussed in [125]. In Figs. 13(a) and 13(b), two samples with different degrees of disorder are shown. Figure 13(a) shows an array with low degree of imperfections in the lattice while Fig. 13(b) displays a sample with low fabrication quality. The presence of the imperfections on individual nanoparticles within the array introduces a large number of locations with inhomogeneously enhanced electric fields in comparison with the perfect lattice, where the electric field is dominated by SLRs [Figs. 13(c) and 13(d)]. As a result of this inhomogeneous field, the radiation pattern of the emission beyond the threshold is significantly modified. In Figs. 13(e) and 13(f), the angle-resolved emission of the PEP laser above the threshold is shown. For the sample with low degree of imperfections a narrow distribution of the emission in the momentum space is observed. However, increasing the density of imperfections leads to a wide spread of the emission momentum [Fig. 13(f)].

10. PERSPECTIVES

We discuss possible future research directions within the field of organic-based exciton-polaritons that could be important steps following the demonstration of PEP condensation.

A. Reduction of the Polariton Lasing Threshold

The research on nonlinear properties of organic-based exciton-polaritons has been mainly focused on the observation of exciton-polariton lasing/condensation. These experiments, as pointed out earlier, utilize amplified femtosecond optical pulses to achieve high enough density of exciton-polaritons necessary for the condensation. Despite the successful observation of phenomena such as condensation and superfluidity using this experimental approach, prospects of applications for organic-based exciton-polaritons pumped by amplified femtosecond pulses seem improbable. To address this limitation, reduction of the exciton-polariton lasing threshold could be vitally important. The efforts toward the reduction of polariton lasing thresholds could be continued along two main directions.

Chemical direction: Designing molecules with strong transition dipole moments, and the possibility of reaching high enough molecular concentrations without quenching and exciton-exciton annihilation, could potentially lead to lower polariton lasing thresholds. In addition, a more comprehensive study of the role of vibrational relaxation in organic-based polariton lasing, and the investigation of the methods that can influence

![Fig. 13. SEM images of samples with 380 nm pitch size along the long axis (a) used in [63] with low density of imperfections. Inset: simulations of the electric field intensity for the lattice without imperfections. (b) Used in [125] with high degree of disorder and imperfections. Inset: simulations of the electric field intensity for the lattice with structural imperfections. The scale bars are 400 nm. Figures reproduced from Ref. [63] and Ref. [125] with permission. Angle resolved PL measurements of the exciton-polaritons above the threshold for the sample (c) without structural imperfections and (d) with structural imperfections.](image)
these processes, could lead to a better understanding of the mechanisms that modify the threshold values.

**Photonic direction:** Designing cavities with high quality factor could potentially lead to lower polariton lasing threshold. Microcavities with quality factors between 100–600 and plasmonic lattices supporting dark modes (modes with suppressed radiative losses) have been used for achieving PEP lasing. The reported polariton lasing thresholds for all these studies are of the same order of magnitude. However, a comprehensive study on the role of cavity losses and resonance quality factors is required to determine the role of optical losses in the process of condensation using organic compounds.

**B. Optical Parametric Oscillation and Amplification**

One appealing aspect related to the nonlinear properties of exciton-polaritons is the possibility of achieving optical parametric oscillation and amplification at relatively low pump fluences [112,113]. Observation of these two phenomena is the result of the excitonic character of exciton-polaritons and their mutual interaction that leads to considerable $\chi^3$ values (third-order nonlinear coefficient). Optical parametric oscillation and amplification has been so far only observed in inorganic exciton-polaritons at low temperatures [111,112,126,127]. As pointed out earlier, the extended wave function associated with Wannier–Mott excitons allows the long-range and effective interactions among them. These interactions are far less significant in organic compounds due to the inherently localized wave function of Frenkel excitons. As a result, the strength of the third-order interactions in organic systems has not been large enough for the observation of optical parametric oscillation and amplification. However, the possibility of incorporating a very high density of molecules within the mode volume of the optical mode defined by SLRs is an advantage that can be utilized to enhance these interactions. Also, using molecules with strong oscillator strength and cavities with higher quality factors, could help for this quest.

**C. Modification of the Photochemical Reactions**

Besides the applications in nonlinear optics, where polaritons are investigated under high fluence pump intensities, the formation of exciton-polaritons in the strong coupling regime modifies materials properties, even in the absence of the light [78]. Historically, modifications to the properties of organic molecules are achieved by synthesizing different molecular structures. Although the possibilities of molecular synthesis are huge, there are limits to the performance of molecular systems. In the strong coupling regime, the modified properties result from the hybridization of excitons with photonic modes in the cavity. As discussed earlier, this hybridization leads to the formation of a lower and an upper polariton band. Due to the hybrid light–matter character, exciton-polaritons have properties that cannot be achieved by chemical synthesis, such as very low effective mass and a delocalized nature [72,73]. These unique properties of exciton-polaritons make strong coupling a promising tool to modify molecular properties, without changing the chemical composition. In the past years, both experimental and theoretical studies have shown enhanced properties of excitons in molecular semiconductors [70,72,79,83,85,86,88,112].

These “proof of principles” underpin the potential of strong coupling as a promising technique for enhancing or suppressing the yield of certain photochemical reactions. Moreover, the open cavity formed by nanoparticle arrays leading to SLRs opens the possibility of exploiting strong coupling from improving the photochemical properties that are pivotal for improved performance of organic solar cells and light-emitting diodes.

As described in this review, arrays of plasmonic nanoparticles can provide a flexible planar platform for novel experiments in nonlinear optics and photochemistry. The ease of fabrication in addition to the possibility of probing of the system over a large spectral range make these arrays an exciting system for future investigations [128,129].

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