Dispersions and light-matter interactions in plasmonic lattices of different geometries

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A metallic nanoparticle array with a periodicity comparable to the single particle resonance can show extremely narrow resonances in its extinction spectrum. This phenomenon is known as the surface lattice resonance (SLR) of the array. In this dissertation we show how the SLRs can influence the emission of light from nearby emitters, leading to amplified spontaneous emission, lasing, or even condensation. In particular, we focus on the effects of the local density of states (LDOS) and of the lattice geometry.

In Chapters 2 the interactions between SLRs and quantum dots (QDs) are studied. We developed a hybrid lithography-functionalization method to efficiently deposit silica-coated QDs onto the near-field regions of plasmonic nanorays. The emission from randomly-oriented QDs were found to couple with the collective SLR mode of the plasmonic lattice, resulting in amplified spontaneous emission (ASE) and a directional light source. The high LDOS of the SLRs, especially at the Gamma-point, significantly enhanced the spontaneous emission rate of the QDs by a factor of 30.

In Chapter 3, we demonstrate for the first time Bose-Einstein condensation (BEC) of SLRs. SLRs can be considered as bosonic excitations, enabling, under suitable conditions, a macroscopic occupation of given modes. We employed a unique measurement scheme that allows to probe the evolution of the SLRs upon propagation. We showed that the interactions between propagating SLR excitations and organic molecules result to gradual decrease in energy of the SLR excitations and, finally, to BEC.

Chapters 4 and 5 of this dissertation introduce work on geometry dependence of the SLRs. We proposed a simple theoretical framework to interpret the dispersions of nanoparticle arrays with different lattice geometries, such as square, hexagonal, and Lieb lattice. This framework allows designing the lattice parameters and tailoring the dispersion. Based on this we fabricated gold nanoparticle arrays in a honeycomb lattice and measured the dispersions at the K-point in the first Brillouin zone edge. Previous works on lasing in plasmonic nanoparticle arrays rely on feedback at the Gamma-point. For the first time, we have observed lasing at the K-points in a plasmonic lattice, with specific polarization properties originating from the lattice geometry.
It was a very fortunate thing for me that Dr. Lei Shi went back to Shanghai during the Christmas holiday in 2012 and we had an overnight discussion there. Because of this coincidence I have had the pleasure to be a member of the Quantum Dynamics group at Aalto University and to work with the people here during the past four years and nine months. I am grateful to everyone who has assisted, supported and helped me moving forward.

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6. Summary

References

Publications
List of Publications

This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals.


Author’s Contribution

Publication I: “Controlling quantum dot emission by plasmonic nanoarrays”

The author did most of the sample fabrication and major part of the optical measurements and was the main writer of the paper.

Publication II: “Geometry dependence of surface lattice resonances in plasmonic nanoparticle arrays”

The author did all the experimental work. The author proposed the theoretical framework to interpret the measurement results and performed all the simulations. The author was the main writer of the paper.

Publication III: “Bose-Einstein Condensation in a Plasmonic Lattice”

The author fabricated all the samples, and performed some of the experiments with coauthors.

Publication IV: “Lasing at the $K$-points of a honeycomb plasmonic lattice”

The author designed and fabricated all the samples and performed most of the experiments and analyzed the data. The author interpreted the results together with coauthors and contributed to the writing of the manuscript.
Author's Contribution
1. Introduction

For several decades plasmonics has been one of the most appealing and active parts of the field of nanophotonics. With the basis on interactions between electromagnetic (EM) field and conduction electrons on metal surface or in metal nanoparticles, plasmonics explores the spatial confinement of EM field and the resulting field enhancement over sub-wavelength dimensions. Having been utilized by the stained glass adorning the medieval cathedrals, plasmonics has now been implemented by various commercial products and physical systems from bio-sensors to Bose-Einstein condensation.

A collective mode may be supported if metal nanoparticles are arranged as an ensemble. Particularly, if the inter-particle separation is on the order of the resonance wavelength, the collective resonance would have quite a narrow linewidth and thus longer lifetime [1]. And the mode is dispersive so that the resonances are directional. Furthermore, the dispersion and resonance both depend on the particle dimensions and array geometries so they are tunable.

The rapid progress in nanofabrication techniques makes nanoparticle arrays with more complex lattice geometries feasible, extending the realm of experimentally studying of their properties. This chapter presents the basic concepts and phenomena that will be further explored in the following chapters.

1.1 Localized excitation – single particle resonance

A plasmon is the quantum of the collective excitation of free electrons in solids. Surface plasmons are electron plasma oscillations near a metal surface that stem from the broken translational invariance in the direction perpendicular to the surface. The charge oscillations are orthogonal to the surface plane and induce at the surface an evanescent EM field which is transverse magnetic (TM). The combined surface plasmon and the induced field are called surface plasmon polaritons (SPPs) [2]. Figure 1.1a shows a schematic of an SPP propagating at the metal-dielectric interface.

The EM field in the direction perpendicular to the surface is evanescent, reflecting the non-radiative nature of SPPs which prevents energy from propagating
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Figure 1.1. SPPs between a metal and a dielectric medium. a. Schematic of the periodic charge density fluctuations within the metal which are accompanied by the electric field. b. The strengths of the fields associated with the SPP mode decay exponentially with distance away from the interface. c. The dispersion curve for SPPs shows the momentum mismatch problem that must be overcome in order to couple light and SPPs together, with the SPP mode (black solid curve) always lying below the light line (black dotted line). Reprinted with permission from ref. [2]

away from the surface. In the dielectric medium above the metal, typically air or glass, the decay length of the field is of the order of half the wavelength of the light, whereas the decay length into the metal is given by the skin depth, as shown in Figure 1.1b. Being vertically evanescent, the SPP mode always lies below the light line, see Figure 1.1c. It means that SPPs have greater momenta than free space photons of the same frequency. This momentum mismatch imposes a challenge in exciting the SPPs by light, and therefore special arrangements, such as the Kretschmann [3] or the Otto [4] configurations, have to be used to compensate the mismatch between the momentum of the free space light and that of the SPP.

Considering a metal nanoparticle instead of a plane stripe, its enclosed surface would result in a resonance at which the EM field is confined surrounding the particle, as shown in Figure 1.2a. Thus it is called localized surface plasmon resonance (LSPR). LSPR has features of field enhancement and sub-wavelength confinement, see Figure 1.2b. The resonant frequency can be tuned via the refractive index of the surrounding medium, the dielectric function of the metal, the size and the shape of the nanoparticles, as shown in Figure 1.2c.

In the case of a homogeneous metallic particle with size much smaller than the light wavelength in the surrounding medium, the interaction between them, e.g. the polarizability and the extinction cross-section, can be analyzed by the quasi-static approximation [7, 8]. Under this lowest-order approximation, the applied EM field would induce a dipole moment inside the nanoparticle of radius \(a\) with a polarizability

\[
\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}, \tag{1.1}
\]

where \(\epsilon\) and \(\epsilon_m\) are the complex permittivities of the particle and medium surrounding the particle, respectively. And the extinction cross-section can be expressed as [9]
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\begin{equation}
C_{\text{ext}} = \frac{9}{c} \epsilon_m^{3/2} V \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_2)^2 + \epsilon_2^2}, \tag{1.2}
\end{equation}

where $V$ is the volume and $\epsilon_1$ and $\epsilon_2$ are the real and imaginary parts of the complex permittivity of the nanoparticle, respectively.

From Equation 1.2, it is apparent that the extinction experiences a resonant enhancement under the condition that $|\epsilon + 2\epsilon_m|$ is minimal. For the case of small or slowly-varying $\text{Im}(\epsilon)$ around the resonance it simplifies to

\begin{equation}
\text{Re}[\epsilon(\omega)] = -2\epsilon_m. \tag{1.3}
\end{equation}

This relationship is called the Fröhlich condition and is associated with the dipole surface plasmon of the metal nanoparticle.

For a sphere consisting of a Drude metal with a dielectric function $\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$ located in air, where $\omega_p$ is the plasmon frequency of the metal, the Fröhlich criterion is met at the frequency $\omega_{\text{LSPR}} = \omega_p/\sqrt{3}$.

The quasi-static approximation describes the optical properties of nanoparticles of dimensions below 100 nm adequately where the nanoparticle is treated as a dipole. For particles of larger size or complicated shape the quasi-static approximation breaks down due to retardation effects. The consequences include the shift of resonance and the occurrence of higher-order resonances [10, 11]. Figure 1.2c shows an example of how colloidal silver particles of different shapes shift in dipolar resonance. Figure 1.3 shows examples of how the higher-order resonances are excited in gold nanowires with different lengths and in elliptical rings.
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Figure 1.3. SEM images (a–c) and corresponding extinction spectra (d) of gold nanowires excited with light polarized along their long axis of 790 nm (a), 940 nm (b), and 1090 nm (c). The length of the short axis and the height are 85 nm and 25 nm, respectively. (e) Extinction spectra of gold elliptical rings with aspect ratio 2.1 for longitudinal (L, red) and perpendicular (S, blue) polarizations and the corresponding charge distributions (f). Numbers at the spectral peaks indicate the order of the multipolar excitation. Reprinted with permissions from ref. [10, 11]

1.2 Collective excitation – surface lattice resonance

We have seen that the LSPR of a single metallic nanoparticle can be excited in the Fröhlich frequency defined by Equation 1.3. In particle ensembles, frequency shifts are expected to occur due to EM interactions between the localized modes. For small particles, these interactions are essentially of a dipolar nature, and the particle ensemble can in a first approximation be treated as an ensemble of interacting dipoles.

In particular, when the inter-particle separation is comparable to the wavelength of single particle resonance, a collective mode, called surface lattice resonance (SLR), will be formed out of the diffractive orders (DOs) of the periodicity and the LSPRs on individual particles [1, 12–16], as shown by the narrow features in the extinction spectra for gold nanorod arrays in Figure 1.4.

The primary reason why SLRs have gained prominence is their combination
Introduction

Figure 1.4. Extinction spectra of gold nanorod arrays with different dimensions and the same periodicity as insets show. The solid and dashed white lines correspond to the (+1, 0) and (−1, 0) DOs, respectively. The non-dispersive resonances on the high-frequency side of the spectra are the dipolar LSPRs for the short axis of the nanorods, whereas the narrower and dispersive resonances below the DOs are the SLRs. Reprinted with permission from ref. [15]

of desirable plasmonic and photonic attributes: high field enhancements characteristic of plasmonic nanostructures with large extended volumes and long-lived lifetimes from the photonic array structure [17]. These advantages make metal nanoparticle arrays apt to manipulate light at the nanoscale. SLRs have been exploited, for example, in light harvesting [18], emission control [19, 20], strong light-matter interaction [21–23], magneto-plasmonic responses in magnetic nanoparticle arrays [24, 25], dark mode excitation in asymmetric dimer arrays [26], super-lattice modes in hierarchical gold particle arrays [27], lasing action [28–33] and, recently, in Bose-Einstein condensation [34, 35].

1.3 Interactions between quantum emitters and plasmonic modes

Many sources of light involve transitions between the electronic energy levels of a well-defined quantum system, such as organic dye molecules, semiconductor materials, or semiconductor nanocrystals (quantum dots, QDs). The basic mechanism of fluorescence or emission is to excite the system to a higher electronic energy state, for instance by absorbing an incident photon or by carrier injection, and then the excited state would decay to the ground state while emitting a photon. The photon that excites the system is usually higher in energy than the photon emitted by the fluorescence due to non-radiative vibrational relaxation (heat) of the excited electronic state.

1.3.1 Fluorescence enhancement – Purcell effect

The transition or decay rate between the eigenstates of a quantum system due to a perturbation is governed by the Fermi’s golden rule:
where $\gamma(r)$ is the modified decay rate at position $r$ in a cavity and $\gamma_0$ its free space value; $\rho$ is its corresponding local densities of state (LDOS). For an emitter placed at the antinode of a cavity at resonance, the decay rate modification corresponds to the Purcell factor:

$$F_P = \frac{3}{4\pi^2} \frac{\lambda^3 Q}{V},$$

where $Q$ and $V$ are the quality factor ($Q$-factor) and mode volume of the cavity, respectively, and $\lambda$ indicates the emission wavelength within the cavity material. Therefore the concentrated EM fields near metallic surfaces due to LSPR and/or SLR can enhance the emission of fluorescent species placed in the near field. But the emission enhancement decreases when the molecule is placed too close to the metallic surface due to fluorescence quenching via non-radiative transitions. Enhancements of the fluorescence emission have been observed from arrays of gold nanorods coated with polymer matrix containing fluorescence dye molecules [19] or a thin layer of randomly oriented core/shell quantum rods [20].

### 1.3.2 Strong coupling

The Purcell effect is irreversible – the energy of the photon cannot be transferred back to the emitter. This regime where Fermi’s golden rule applies is referred to as weak coupling regime, and Purcell effect describes fluorescence enhancement in that regime. On the other hand, strong coupling happens when energy exchange rates of the interacting entities are faster than loss rates. Energy exchange in time leads to a splitting of the resonant energy called Rabi splitting [21]. Strong coupling has been observed in silver nanoparticle arrays with high concentrations of dye molecules [21, 22, 36] and the resulting hybrid mode was found to be spatially coherent [23].

### 1.3.3 Lasing and condensation

The three principal elements of a laser device are an energy source (pump), a gain medium and an optical resonator that provides feedback. A periodic structure that supports a mode with zero group velocity at a band edge can work as a resonator [37]. Plasmonic arrays supporting SLRs are ideal platform for nanoscale lasing because of their ultra-narrow linewidths and sub-wavelength localized field enhancements around the nanoparticles [13, 14, 38]. Lasing action relying on plasmonic lattice has been observed in gold and silver nanoparticle arrays embedded in polymer matrix containing dye molecules [29, 39] and in organic solvents filled with molecules [31], and from dark mode out-coupling due to the finite size of nanoparticle arrays [32], and multi-modal lasing was found by superlattice SLRs in hierarchical nanoparticle arrays [40]. For further
examples see refs. [17, 41].

Bose–Einstein condensation (BEC) is a remarkable manifestation of quantum statistics and macroscopic quantum coherence. While ultracold quantum gases have provided condensates close to the original ideas of Satyendra Bose and Albert Einstein in equilibrium system [42–44], the exciton-polaritons, which are strongly coupled from excitons and cavity photons, have shown condensation in non-equilibrium systems [45–55]. Other condensation phenomena in non-equilibrium systems include the spin-wave excitations in magnetic materials [56, 57] and photons in microcavities [58–60]. In plasmonic nanoparticle arrays, strong light–matter interaction between excitons and SLRs can also produce hybrid light–matter quasiparticles [21] which has opened possibilities for strongly coupled condensates [33]. On the other hand, a realization of SLRs BEC in the weak coupling regime was also proposed [34], and recently observed (see ref. [35] and Publication III of this dissertation).
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2. Spectral modulation of quantum dots by plasmonic nanorod arrays

The surface chemical properties of QDs facilitate the control and modification of their positions precisely. In the case of the silica-coated core/shell QDs [61], we have developed a lithography-functionalization hybrid approach to assemble the QDs on top of silver nanoparticles, ensuring a near-field coupling between QD emission and the plasmonic modes. Angle-resolved extinction and emission spectra have been measured to characterize the nanoarrays and the functionalized QDs. Features of the SLRs are clearly visible from the emission spectra. Lifetime measurements have further indicated that the spontaneous emission decay rate of the QDs is enhanced. Finite-difference time-domain (FDTD) simulations have been performed to reveal the origin of emission enhancement.

2.1 Sample fabrication

A common procedure to prepare a nanoparticle-deposited surface is to employ a self-assembled monolayer (SAM) of bi-functional molecules to bond the nanoparticles onto the interface, called a surface modification or functionalization process [62–64].

Organofunctional silanes are commonly used to modify the surface of silica [65]. They have been developed since the 1950s and hold their ability to act as a coupling agent due to one organofunctional group, −R, and three hydrolysable groups, −X, as shown in Figure 2.1a. One of the ideal candidates is trialkoxysilanes, which can be hydrolyzed in water, forming reactive silanetriols [66], see Figure 2.1b. The reactive silanetriols can later condense to the hydroxyl group of silica surface via siloxane bonds, as shown in Figure 2.1c. This functionalization process creates a broad field of both industrial and analytical applications. For instance as illustrated above, the condensation reaction of an organofunctional trisilanol to a silica surface offers the possibility of introducing hydrophobic and/or hydrophilic groups to the surface, depending on the properties of the organofunctional group, −R.

Our goal is to deposit silica-coated QDs on silver nanoparticle arrays with precisely controlled positions, i.e., in the near-field vicinity of nanoparticles, to
ensure a deterministic coupling between the emitters and the plasmonic modes. The high affinity of thiols for the surfaces of noble metals can generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at the exposed interface [68, 69], as shown in Figure 2.1d. The properties of SAMs derived from the adsorption of alkanethiols on silver and other metals have been extensively studied [70–72].

In order to deposit the QDs on top of silver nanoparticle array, (3-Mercaptopropl) trimethoxysilane (3-MPTS) is chosen to work as the linker molecule between the silver surface and the QDs silica shell. The strong covalent bond between thiol group in the molecule and silver can first form a SAM of 3-MPTS on the metal surface, with trimethoxysilane tails outward [73]. The silanetriol-terminated molecules can then connect with the hydroxyl groups on the silica after hydrolysis [74].

The fabrication process is shown in Figure 2.2. A layer of 200 nm of poly(methyl methacrylate) (PMMA) is spin-coated on a cleaned fused silica substrate, and 10 nm of aluminum is evaporated as a conductive layer (not shown in the schematic).
The nanoparticle arrays are designed to have a size of $100 \times 100 \, \mu m^2$. Each particle has a rod shape of $d_y = 65 \, nm$, $d_x = 0.6 \, p_x$ and the array has a periodicity of $p_y = 200 \, nm$ along the $y$-axis and $p_x$ along the $x$-axis varies from 350 to 500 nm.

The defined patterns are exposed by e-beam lithography (Vistec, EPBG5000pES). The aluminum is etched with sodium hydroxide aqueous solution. The PMMA is developed with a MIBK : IPA (1 : 3) solution. Then 2 nm of titanium and 30 nm of silver are evaporated on top.

The functionalization process involves immersing the obtained glass slide into 40 mM 3-MPTS solution in ethanol for 72 hours in order to form the 3-MPTS SAM on silver surface; rinsing the slide with ethanol and immersing it into 10 mM sodium hydroxide aqueous solution for 4 hours to hydrolyze the 3-MPTS molecules; finally immersing the substrate into 0.25 µM silica-coated QD suspension for 48 hours to immobilize the silica shell of QDs onto the silanetriols-terminated SAM of the substrate.

Eventually, the PMMA and the metal film (together with the linkers and QDs) on top are removed by a lift-off procedure where the sample is vertically immersed into acetone for 2 hours. The QDs that deposit on the rear side of the wafer are then removed by wiping with acetone for several times using cotton rods. Therefore, we get a sample with a monolayer of QDs deposited only on top of nanoparticles, i.e., the near-field regions of the plasmonic modes, so that the emission from QDs and the collective modes supported by nanoparticle arrays can be sufficiently coupled with each other.

To characterize the functionalization process, atomic force microscope (AFM)
images of both reference non-functionalized and functionalized silver nanoparticles are taken, as shown in Figure 2.3. The obtained cross-sections show that the maximum height of functionalized particles is more than 30 nm higher compared with the non-functionalized particles, and the average diameter of the silica-coated QDs is ~35 nm [61]. This demonstrates the presence of QDs on top of the functionalized particles.

2.2 Angle-resolved spectra of plasmonic arrays with/without QDs

It is imperative to have experimental access to angle- or $k$-resolved information when working with periodic structures, as the DOs of the periodic structures are formed by constructive interference from multiple scattering events in predefined directions. In addition, the dispersion of the supported mode can be revealed from an angle-resolved spectrum.

2.2.1 Measurement setup

To obtain the dispersions of the samples, a Fourier-space measurement setup was developed in our lab [23]. The principle of the setup is to focus the back focal plane image (namely Fourier image, the image that contains the angle information) of the microscope objective into the entrance slit of spectrometer, as shown in Figure 2.4. In this way the projected back focal plane containing $k_{\parallel}$ information can get through and be diffracted by a grating inside the spectrometer, and be further imaged onto a 2D CCD camera ($400 \times 1340$ pixels). Under this configuration each pixel row on the obtained image corresponds to a certain incident angle and every column corresponds to a wavelength resolved by the grating. Therefore the dispersion can be obtained by calculating the in-plane wave vector $k_{\parallel} = 2\pi \sin \theta / \lambda$ at each pixel, where $\theta$ is the angle between the incident light and the sample normal. In this chapter the parallel direction corresponds to the x-axis on the sample.
For the extinction measurement, the sample is illuminated by a halogen lamp and the arrays are embedded in a uniform surrounding medium by covering the array with index matching oil (refractive index $n = 1.4766$) and another fused silica slide. The polarization of the incident light is set to probe the short axis of the nanoparticles. The extinction is defined as $1 - T$, where $T$ is the transmittance of the structure $T = T_{\text{in}}/T_{\text{out}}$, $T_{\text{in}}$ is the transmission through the array and $T_{\text{out}}$ is the transmission in the region outside the array.

![Figure 2.4. Schematic of the Fourier-space measurement setup. A set of lenses are used to focus the back focal plane image of the microscope objective to the slit of the spectrometer. The shades in red indicate the real space path of light through a focused microscope objective and the blue arrows refer to the path in Fourier space. The shade in green is the laser light for emission measurement. An iris pinhole is mounted on the real focal plane for spatially selecting the area of measurement. Reproduced from Publication I with permission.](image)

In order to measure the emission spectra, a pulsed laser beam with a central wavelength of 508 nm and average power of 1.15 mW is used to illuminate the sample. The laser light is filtered out by a dichroic mirror and a linear polarizer is placed in front of the spectrometer so that only the TE-polarized (with electric field component $E_y$) emission can be detected. The emission (photoluminescence, PL) spectrum is then calculated by $\text{PL} = I_{\text{in}} - I_{\text{out}}$, where $I_{\text{in}}$ is the emission intensity from the array and $I_{\text{out}}$ is the emission intensity from outside the array.

### 2.2.2 Results

The SLR dispersions supported by the arrays are revealed by the extinction spectra of the bare particle arrays, as shown in Figures 2.5(a)-(c). The narrow
linewidth indicates the advantage of high Q-factor of the SLR modes. And the lowest orders of SLR dispersion follow well with the (+1, 0) and (−1, 0) DOs in Rayleigh condition [75, 76]. The (+1, 0) and (−1, 0) DOs cross with each other at $k_x = 0$, namely, the band edge at the Γ-point.

![Image](image.png)

**Figure 2.5.** Extinction spectra from non-functionalized arrays: (a) $p_x = 365$ nm; (b) $p_x = 415$ nm; (c) $p_x = 435$ nm; and emission spectra from functionalized arrays with the same periodicities (d)-(f). The inset of (f) shows the normalized emission spectrum of colloidal QDs. Reproduced from Publication I with permission.

The emission spectra of the functionalized arrays with the same periodicities remarkably well follow the SLR dispersions of bare arrays, as shown in Figures 2.5(d)-(f). The emission is especially amplified in the resonant locations overlapping with colloidal QDs emission spectrum, as shown in the inset of Figure 2.5(f). In particular, when the QD emission maximum coincides with the Γ-point of the SLR dispersion (for array $p_x = 415$ nm), the emission becomes overwhelmingly normal to the sample surface. Therefore, upon coupling to the SLR mode, the QD emission change into directional light source.

### 2.3 Decay rate of QDs coupled to plasmonic arrays

The emission decay rate of QDs is measured using a time-correlated single-photon counting (TCSPC) setup. The TCSPC setup includes a set of instruments that can accept the sparseness of the collected photons and reconstruct the
fluorescence decay profile from the multitude of single photon events collected over many cycles. The method is based on the repetitive, precisely-timed registration of single photons of, e.g., a fluorescence signal [77, 78]. Provided that the probability of registering more than one photon per cycle is low, the histogram of photon arrivals per time bin represents the time bin from a “single shot” time-resolved analog recording.

### 2.3.1 Measurement setup

![Figure 2.6. Schematic of emission decay rate measurement with TCSPC setup. Inset: an obtained decay histogram.](image)

Figure 2.6 depicts the schematics of the measurement setup. The sample is excited by the same pulsed laser of 508 nm. The pulse width is about 500 picoseconds and the repetition frequency is 5 MHz. The emission is passing through a band pass filter (617/73 nm) before focusing into a single-photon detector (SPD). The TCSPC acquisition card is connected with SPD while the other channel is synchronizing with the laser head. A decay histogram is obtained after a few minutes acquisition time, as shown in the inset of Figure 2.6. Then the decay rate is extracted by an exponential fitting procedure. For a complex system the parameters of each component can be extracted by a multi-exponential decay curve fitting, with deconvolution of the instrument response function (IRF).

### 2.3.2 Results

The decay kinetics of a system is expressed as the sum of the exponential decay terms contributed by each component, combined with convolution with the IRF of the measurement instrument:
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\[ I(t) = \text{IRF} \otimes \left[ \sum_i A_i \exp\left(-\frac{t}{\tau_i}\right) \right], \quad (2.1) \]

where \( A_i \) and \( \tau_i \) are the amplitude and decay time for each component, respectively. The averaged fluorescence decay time is obtained as the weighted mean value of each component [78, 79]:

\[ <\tau> = \left( \sum_i A_i \tau_i \right) / \left( \sum_i A_i \right). \quad \text{(2.2)} \]

For uncoupled QDs immersed in the index-matching oil on a glass substrate, the measured histogram is a single exponential decay curve, as shown by the black curve in Figure 2.7.

![Figure 2.7](image)

**Figure 2.7.** Normalized emission decay curves for QDs embedded in index matching oil (black curve) and for QDs coupled with the plasmonic nanoarrays with the periodicity \( p_x = 400 \text{ nm} \) (blue curve) and \( p_x = 415 \text{ nm} \) (red curve). Reproduced from Publication I with permission.

The decay becomes much faster for QDs on the arrays, as shown by the blue (\( p_x = 400 \text{ nm} \)) and red (\( p_x = 415 \text{ nm} \)) curves in Figure 2.7. After fitting with Equation 2.1 and taking the average value according to Equation 2.2, the black curve fits well with a single exponential decay with an obtained decay time \( \tau_0 = 14.51 \text{ ns} \). The averaged decay times for blue and red curves are \( \bar{\tau} = 4.43 \text{ ns} \) and \( \bar{\tau} = 4.19 \text{ ns} \), respectively. The enhancement factors are therefore 3.28 for \( p_x = 400 \text{ nm} \) and 3.46 for \( p_x = 415 \text{ nm} \).

The faster decay rate is due to the Purcell effect [80], namely the change of the LDOS near the QDs. The high LDOS of SLR in the vicinity of nanoparticles leads to the quicker emission from QDs.
2.4 FDTD simulations of emitters coupled with plasmonic arrays

In order to support the interpretation of the experimental results, FDTD simulations are performed (FDTD Solutions, Lumerical) for the hybrid systems – first an emitter with a single particle, then emitters with an array of particles.

2.4.1 A dipole coupled with a single nanoparticle

To explore the coupling mechanism between an emitter and an individual particle, a hybrid system composed of an electric dipole source with a single silver nanorod in a homogeneous refractive index \(n = 1.48\) is simulated, as shown in Figure 2.8(a). The nanorod has a length of \(d_x = 200\) nm, a width of \(d_y = 65\) nm, and a height of \(h = 30\) nm (with 2 nm of titanium below). The simulation area is all surrounded by perfectly matched layer (PML) boundary conditions. The electric dipole source is 10 nm above the silver particle.

Dipoles with x-, y- and z-orientations are simulated and the corresponding decay rate enhancements are shown in Figure 2.8(b). Figure 2.8(c) shows the simulated extinction spectra of the nanorod under a plane wave polarized along the x-axis with normal and in 30\(^\circ\) incidence, where the resonances are at \(\lambda = 520\) nm and \(\lambda = 660\) nm, respectively. They are related to the 2\(^{nd}\) and the 3\(^{rd}\) order.
longitudinal LSPRs [10, 81]. The decay rate enhancements in Figure 2.8(b) are therefore due to the coupling with the higher order longitudinal LSPRs.

### 2.4.2 Dipoles coupled with nanoparticle arrays

To simulate the coupling between emitters and nanoparticle arrays, periodic boundary conditions are set along the x- and y-axes, as shown in Figure 2.9(a). The lattice periodicities along the x- and y-axes are in line with the fabricated structures. The normalized decay rate enhancement here is calculated as:

\[
\frac{\bar{\Gamma}}{\Gamma_0} = \frac{\Gamma_x + \Gamma_y + \Gamma_z}{3\Gamma_0},
\]

where \(\Gamma_x\), \(\Gamma_y\) and \(\Gamma_z\) are the simulated decay rates along three dipole orientations.

![Figure 2.9](image)

**Figure 2.9.** (a) Schematic view of the simulation configuration for the calculation of the decay rate enhancement of dipoles coupled with an array of silver nanorods. (b) Calculated decay rate enhancements of the dipoles coupled with nanoparticle arrays for two lattice periodicities \(p_x = 400\) nm and \(p_x = 415\) nm. Reproduced from Publication I with permission.

The simulated average decay rate enhancements for two lattice periodicities, \(p_x = 400\) and \(p_x = 415\), are shown in Figure 2.9(b). The maximum decay rate enhancement for \(p_x = 400\) nm reaches 75 at \(\lambda_{em} = 585\) nm and for \(p_x = 415\) nm reaches 60 at \(\lambda_{em} = 608\) nm, which is the same wavelength as QD emission peak.

The obtained decay rate enhancements from measurements are lower than the simulation maxima. This is due to 1) the experimental values are measured within a broad wavelength regime (617 ± 37 nm) while in the simulations all the values are calculated monochromatically, and 2) in the simulations all the dipoles are placed in specified positions (10 nm on top of particle) while in the experiments their relative positions fluctuate.

To estimate the radiative decay rate enhancement of the emitters coupled with the array, the radiative power of the simulation area is divided by the power emitting from the dipoles, to calculate the quantum yield (\(\eta\)):

\[
\eta = \frac{\Gamma_{\text{Radiative}}}{\Gamma_{\text{Total}}} = \frac{P_{\text{Radiative}}}{P_{\text{Total}}}. \tag{2.4}
\]

With an assumption that the intrinsic quantum yield of QD is 1, the calculated
quantum yields for dipoles on top of nanoparticle arrays with periodicities $p_x = 400$ nm and $p_x = 415$ nm are 10% and 50% at $\lambda_{em} = 608$ nm, respectively. With a decay rate enhancement of 60 and a quantum yield 50%, the radiative decay rate of the hybrid system is therefore enhanced by a factor of 30 at the emission maximum.

2.5 Conclusion

In this chapter, we have demonstrated a functionalization method to deposit silica-coated QDs into the near-field regions of plasmonic nanoarrays. The method can be regarded as an adequate approach to tailoring the emission profile of nanoscale emitters and related coherence phenomena in general.

With an angle-resolved spectrometer setup, we have measured the extinction and emission spectra from both non-functionalized and functionalized arrays. We find that the spontaneous emission of QDs is amplified and following the SLR dispersions of the plasmonic array. Furthermore, lifetime measurements reveal that the emission decay rate of QDs is enhanced upon coupling with the SLR mode, especially when the emission maximum closes to the $\Gamma$-point. The numerical simulations confirm the capability of the plasmonic mode to enhance the emission.
3. Bose-Einstein condensation in a plasmonic lattice

Some quasiparticles, particles that are effective descriptions of excitations, have integer spins and can be expected to obey Bose–Einstein statistics like bosonic particles. Therefore a BEC can occur for quasiparticles. As introduced in Chapter 1, exciton-polaritons, magnons and photons have integer spin which means they are bosons that can form condensates. In this chapter we briefly present our work on experimental observation of plasmonic BEC in room temperature, in particular, the author’s contributions on sample fabrication and optical measurements.

Note that from this chapter on, the measured in-plane wave vector \( k_\parallel \), namely the direction parallel to the spectrometer slit, is along the y-axis of the sample structure, due to an updated measurement setup.

3.1 Sample fabrication

The lifetimes of plasmonic modes are only on the order of 100 femtoseconds. This poses major challenges for reaching a macroscopic population in these systems. Indeed, the thermalization timescales need to be 2–3 orders of magnitude shorter than in photon condensates in optical cavities. Another challenge is to probe the dynamics of such a fast system. In order to overcome these challenges, we fabricate gold nanoparticle arrays with different periodicities and layout dimension of \( 100 \times 300 \ \mu m^2 \), as shown in the scanning electron micrograph (SEM) in the inset of Figure 3.1. And a unique measurement scheme is developed to probe the evolution of the supported SLRs upon propagation, which will be discussed in the next section.

The rod-shaped gold nanoparticles are fabricated on a borosilicate substrate by electron-beam lithography and subsequent electron-beam evaporation of 2 nm of titanium and 50 nm of gold. The square lattice periodicity is designed to vary from 580 nm to 610 nm. The width of individual nanoparticle is fixed to 100 nm and the length is chosen to be 65% of the periodicity. Under this filling fraction a band-gap is formed sufficiently near the crossing of the DOs at the \( \Gamma \)-point.
The plasmonic nanoarray is overlaid with dye molecules, in a 50 mM concentration solution of IR-792 perchlorate dissolved into 1:2 (dimethyl sulfoxide)/(benzyl alcohol) solvent. While measuring, the dye molecules are pumped at the edge of the array and the spectral evolution of SLR excitations propagating along the array is recorded, as shown in Figure 3.1.

![Figure 3.1](image)

**Figure 3.1.** The experimental scheme, the dye molecules are pumped at the edge of the array (the purple arrow) and the spectral evolution of SLR excitations propagating along the array is recorded. The inset shows the SEM of a part of the array, where the scale bar is 300 nm. Reproduced from Publication III with permission.

### 3.2 Measurement setups

To characterize the thermalization process of the system and identify the condensation, angle-resolved spectra, spatial-resolved spectra and spatial coherence (with both double slit and Michelson interferometer) measurements are performed. Also a pump-probe measurement was performed but is not described here as the author did not participate in it.

Angle-resolved transmission spectra are obtained by focusing light from a halogen lamp onto the sample and collecting the transmitted light with a microscope objective (10×, 0.3 NA), as shown in Figure 3.2a. Similar to Chapter 2, the back focal plane of the objective is focused to the entrance slit of the spectrometer. The $E(k_{\parallel})$ dispersion is subsequently calculated from the angle and wavelength-resolved spectra as $E = \frac{hc}{\lambda}$ and $k_{\parallel} = k_0 \sin \theta$, where $k_0 = \frac{2\pi}{\lambda}$ and $\theta$ is the angle with respect to the sample normal and $\lambda$ is the wavelength.

For emission measurements, femtosecond laser pulses (100 fs pulse duration, 750 nm central wavelength, 1 kHz repetition frequency, microjoule pulse energy) are directed through a pinhole and focused to the sample via a lens and a mirror. An iris is used to spatially filter the light emerging from the sample. For the double slit experiment, the iris is replaced by a double slit (90 µm inter-slit distance and 30 µm slit width).
For spatially resolved spectra, the real-space image of the sample is focused to the spectrometer entrance slit, by placing an additional lens in front of the spectrometer, as shown in Figure 3.2b.

To measure the spatial coherence of the BEC on the sample, the spectrometer is replaced by a Michelson interferometer, as shown in Figure 3.2c. The beam splitter is rotated by 90°. One output arm of the beam splitter is directed to a hollow roof L-shaped mirror in order to invert y coordinate to −y upon reflection. The other output arm is reflected back from a regular mirror mounted on a delay stage. Both beams are then directed through the beam splitter. A lens is used to focus both real space images (the inverted and the original one) to a charge-coupled device (CCD) camera.

![Figure 3.2](image_url)

**Figure 3.2.** Schematics of the different measurement setups. (a) Angle and energy-resolved measurement; (b) spatial and energy-resolved measurement; and (c) Michelson interference measurement. Reproduced from Publication III with permission.

### 3.3 Results and discussions

By pumping the dye molecules at the edge of array and measuring the spatial-resolved spectra, the spectral evolution of supported SLR excitations propagating
along the array can be recorded. Three arrays with periodicities $p = 580$ nm, $p = 610$ nm and $p = 600$ nm show distinctive spectra, see Figures 3.3a-c, due to the relative energy position of SLR band edge of the array at the $\Gamma$-point with respect to the absorption edge of the dye molecules $\xi_{\text{abs}} \approx 1.34$ eV, at which the absorption rate is effectively zero (small compared to the loss rate).

Figure 3.3. The measured spatially resolved spectra of the emission show a crossover from thermalization to lasing to BEC. Reproduced from Publication III with permission.

In the case of $p = 580$ nm, as shown in Figure 3.3a, the SLR band edge energy (dashed line) is well above $\xi_{\text{abs}}$ (solid line). The dye molecules offer a bridge over the band gap, as photons are absorbed from the energies of the upper dispersion branch and emitted to the lower one. Eventually the redshift saturates to a broad spectral range at 1.34 eV, where the absorption has ceased.

When the band edge is lower in energy than $\xi_{\text{abs}}$ (corresponding to the case of $p = 610$ nm), the absorption–emission cycles causing the red-shift are suppressed near the band edge. The narrower linewidth, together with a nonlinear pump dependency with a clear threshold, is characteristic for lasing, which is similar to that reported before in almost identical systems but pumping over the whole array [29, 32, 33].

When the band edge is matched with $\xi_{\text{abs}}$, the absorption–emission cycles are possible until the band-edge energy and thermalization takes place. A macroscopic occupation emerges when the thermalizing population reaches the band edge. With further measurements using the setups introduced in the previous
section, it is shown that the population follows a Bose-Einstein distribution with macroscopic occupation of the ground state and a thermalized tail. Moreover, a sharp increase in temporal coherence (evidenced by linewidth narrowing) and a build-up of spatial coherence are found. The observed phenomena fulfill the main characteristics of BEC. A more detailed discussion and interpretation can be seen in Publication III.

The lasing and BEC measurements are distinct in how the relative intensities of the band edge and the rest of the population at higher energies evolve along the array. In the lasing case, as shown in Figure 3.3e, a lasing peak is generated at the pump spot and then spreads through the array. On the other hand, in the BEC case, the population at the band edge is in the beginning negligible, and upon propagating the population is accumulated to the ground state via thermalization, as shown in Figure 3.3f.
Bose-Einstein condensation in a plasmonic lattice
4. SLRs on plasmonic nanoarrays with different lattice geometries

So far, most of the investigations and implementations of SLRs have been based on square or rectangular lattices and near the Γ-point. The unexplored realms, i.e., the SLR modes supported by nanoparticle arrays with different geometries and the properties beyond their Γ-points, may show new interesting phenomena and potential applications. From this chapter on, we present the effects and phenomena stemming from lattice geometry, first showing the SLR dispersions of different lattice geometries in Chapter 4, and then the specific mode properties at the \( K \)-point in a plasmonic honeycomb lattice as well as the \( K \)-point lasing measurements in the next chapter.

The lattice geometry plays an important role on the supported SLRs in a plasmonic array, because the radiative coupling between neighboring dipoles depends not only their separations but also on their spatial arrangement in the two dimensional plane, as shown in Figure 4.1. However this dependence has not been systematically studied hitherto. Previous work has investigated the influence of lattice symmetries on SLRs by measuring the normal incident extinction spectra of square, hexagonal, honeycomb and rectangular arrays. Their extinction spectra were found with no much difference at \( k_\parallel = 0 \) – no one showed a clear advantage over the others in terms of linewidth. And the spectra of lattice with high degree of symmetry (square, hexagonal and honeycomb) are insensitive to the polarization angle [82]. However, things might be different if we look at the dispersions – concern over a range of in-plane wave vector, by performing an angle-resolved spectra measurement.

To investigate this, we fabricate arrays with different geometries and analyze their corresponding SLR dispersions. Angle-resolved extinction spectra are measured for both TE- and TM-polarized light. The measured spectra indicate different SLR dispersions among these lattices. TE- and TM-polarized modes also show distinct dispersions for the same lattice type. We interpret these as consequences of different contributions from the lowest DO wave vectors and their angles with the in-plane dipole orientations on the individual nanoparticles. FDTD simulations of field distributions are also performed for a square lattice to corroborate our interpretation.
4.1 Theoretical framework

As explained in Chapter 1, SLR involves a collectively scattered field that comprises components produced by scattering from all particles of the array [1]. The collective scattering property can be obtained by a sum of phase differences from all the individual particles:

$$A_{\text{sum}} \propto \sum_l \exp(i\vec{s} \cdot \vec{r}_l),$$  \hspace{1cm} (4.1)

where $A_{\text{sum}}$ is the amplitude of overall scattered light, $\vec{s} = \vec{k} - \vec{k}_0$ is the difference between incoming and outgoing light of each particle, as shown in Figure 4.2, and $\vec{r}_l$ is the location of each particle. In the case of a 2D Bravais lattice, where $\vec{r}_l = n_1\vec{a}_1 + n_2\vec{a}_2$ and $\vec{a}_1$ and $\vec{a}_2$ are the primitive vectors of the lattice, $A_{\text{sum}}$ is always zero except when $\vec{s}$ corresponds to a reciprocal lattice vector $\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2$ where $\vec{b}_1$ and $\vec{b}_2$ are the primitive vectors in the reciprocal space.

If the lattice contains more than one particles in a unit cell (a basis), as the dotted circles show in Figure 4.2, the overall scattered light involves also the contributions from particles in the basis:

$$A_{\text{sum}} \propto \sum_l \sum_b \exp\left[i\vec{s} \cdot (\vec{r}_l + \vec{r}_b)\right]$$

$$= \left[\sum_b \exp(i\vec{s} \cdot \vec{r}_b)\right] \cdot \left[\sum_l \exp(i\vec{s} \cdot \vec{r}_l)\right]$$ \hspace{1cm} (4.2)
The term $[\sum_b \exp(i\vec{s} \cdot \vec{r}_b)]$ modifies the magnitude and/or phase of the scattered light, thus can be called the *envelope factor*.

![Figure 4.2](image)

**Figure 4.2.** Scattering of a plane wave by a 2D particle array. Here $\vec{k}_0$ and $\vec{k}$ indicate the incoming and outgoing wave vectors, respectively, and $\vec{s} = \vec{k} - \vec{k}_0$ denotes the scattering vector. Reproduced from Publication II with permission.

The dispersion for a DO, namely the light propagating along a lattice surface, follows the Rayleigh condition [75, 76]:

$$\frac{\omega}{c} = |\vec{k}_\parallel + \vec{G}|,$$

(4.3)

where $\vec{k}_\parallel$ is the in-plane wave vector. According to the discussion above, if there are multiple particles in the unit cell, the DO still has the same dispersion with the resonance modified by an *envelope factor* $[\sum_b \exp(i\vec{s} \cdot \vec{r}_b)]$. The overall wave vector $(\vec{k}_\parallel + \vec{G})$ also indicates the propagation direction of a certain mode so one should take into consideration the relation between this direction and the radiative pattern of single electric dipole by each nanoparticle.

### 4.2 Sample fabrication and optical characterization

To examine the influence of lattice geometries on SLR dispersions, silver nanoparticle arrays are fabricated on borosilicate glass with different patterns by e-beam lithography. Square, hexagonal, rectangular, 45° rotated square, honeycomb and Lieb lattices are designed for comparison, as shown in the top-view scanning electron micrographs (SEMs) in Figure 4.3. Each array has a size of 100 × 100 μm² and each silver cylinder has a height of 30 nm and a diameter of 60 nm, with 2 nm titanium below as an adhesive layer. The nearest particle separations of the arrays are chosen such that the $\Gamma$-points of all lattices are at the same frequency.

Similar to the previous chapters, the angle-resolved extinction spectra are measured by focusing the image of the back focal plane of the microscope objective (10×, 0.3 NA) to the entrance slit of the spectrometer, as shown in the schematic Figure 3.2a. Here a white light-emitting diode (LED) is used as a light source and a polarizer is placed in the detection path to control the detected...
polarization. The sample slide is immersed in an index-matching oil (refractive index $n = 1.52$) and covered by another borosilicate glass slide. The extinction spectra of the sample are then obtained by $1 - T$.

### 4.3 Measurement results

#### 4.3.1 Square lattice

Figures 4.4(b) and 4.4(c) show the extinction of a square lattice with a periodicity of 375 nm for TE- and TM-polarized detections, respectively. The supported SLR modes are clearly seen from the narrow features, while the broad non-dispersed features (~2.4 eV) are LSPR of individual particles. The SLR modes are dispersed quite differently though they have the same Γ-point positions. The different dispersions among the TE- and TM-modes originate from the different mode vectors of the lowest DOs on square lattice, as shown in Figure 4.4(a). The four lowest DO vectors, namely $\mathbf{k}_{DO} = \mathbf{k}_|| + \mathbf{G}$, have the same magnitude when $\mathbf{k}_|| = 0$. This means the DOs are degenerate at normal incidence, propagating either along the x- or y-axis.

The light incident with an angle will equivalently add an in-plane wave vector $\mathbf{k}_y$ to the DOs and their magnitudes become then different. The orders $(0,1)$ and $(0,-1)$ are parallel to $\mathbf{k}_y$ so both are linearly dispersed, with the opposite slopes. However the order $(1,0)$ and $(-1,0)$ are orthogonal to $\mathbf{k}_y$ so they become hyperbolically dispersed, with the same magnitude, meaning they are still degenerate. On the other side, as discussed in Section 4.1, $\mathbf{k}_{DO}$ also rules the propagation directions of the mode. If the direction is orthogonal to the radiative
Figure 4.4. (a) The schematic of a square lattice in reciprocal space and the four lowest DOs (black arrows). The DOs (0,1) and (0, -1) have been slightly shifted horizontally to be better distinguished. The fuchsia arrows indicate the electric polarizations for TE and TM modes (TE and TM are defined with respect to $k_y$). The measured extinction spectra for (b) TE- and (c) TM-polarized lights. Dashed and dotted white lines represent the calculated DOs (0,1) and (0, -1), respectively. The dashed red line represents the calculated degenerate DOs (1,0) and (-1,0). Reproduced from Publication II with permission.

pattern of individual particle dipoles, as illustrated in Figure 4.1(a), the DO mode will be suppressed.

The combined effects of DOs vectors and radiative patterns are that the (0,1) and (0, -1) DOs are visible with TE-polarized detection (only $E_x$ can pass) because the radiative pattern of $E_x$ oriented dipole is parallel to the y-axis; but they are suppressed with TM-polarized detection (only $E_y$ can pass) due to the absence of radiative coupling. Reversely, the degenerate (1,0)/(-1,0) DOs can be clearly seen with TM-polarized detection, but not visible with TE-polarized detection. In the current measurement an objective with NA = 0.3 is used, which means that at visible regime the maximum detected in-plane wave vector $k_\parallel \sim 4 \times 10^6$ m$^{-1}$. For a square lattice with 375 nm periodicity, the lowest reciprocal lattice vector is around $1.7 \times 10^7$ m$^{-1}$. It means that angle between the largest detectable (1,0) DO vector and x-axis, $\theta$, is less than 14°. The angles between the radiative pattern of $E_x$ oriented dipole are too large to induce sufficient coupling. Therefore they are not observable in the measurement.

As the crossing point of the lowest DOs, namely the $\Gamma$-point, is comparable with and slightly lower in energy than LSPRs of individual particles, the SLRs are quite narrow and follow well with the calculated DOs, see the dashed lines in Figures 4.4(b) and 4.4(c).

4.3.2 Hexagonal lattice

A hexagonal lattice has six lowest DOs, as shown in the schematic in Figure 4.5(a). The higher symmetry results in more features, see the extinction spectra of a hexagonal lattice with a nearest separation of 433 nm in Figures 4.5(b) and 4.5(c). Note here that under the fabricated arrangement, see Figure 4.3(b),
the measured in-plane wave vector $k_y$ is along the $\Gamma - M$ direction in the first Brillouin zone of a hexagonal lattice. The six lowest DOs can be divided into three categories: the linearly dispersed DOs $(1, 1)$ and $(-1, -1)$ (with also the opposite slopes); the degenerate DOs $(1, 0)/(0, 1)$; and the degenerate DOs $(0, -1)/(-1, 0)$. The category one are propagating along the y-axis so are visible only in TE mode measurement, similar with the arguments for the DOs $(0, 1)$ and $(0, -1)$ in a square lattice. The categories two and three are propagating neither along x- nor y-axis so they are visible in both TE- and TM-modes.

![Figure 4.5](image_url)

**Figure 4.5.** (a) The schematic of a hexagonal lattice in reciprocal space and the six lowest DOs. Measured extinction and calculated DOs for (b) TE- and (c) TM-polarized light. Dashed and dotted white lines represent the DOs $(1, 1)$ and $(-1, -1)$, respectively. Dashed and dotted red lines represent the degenerate DOs $(1, 0)/(0, 1)$ and $(0, -1)/(-1, 0)$, respectively. Reproduced from Publication II with permission.

### 4.3.3 Rectangular lattice

The lower symmetry in a rectangular lattice leads to unequal $\Gamma$-points in TE- and TM-modes, as its lowest order lattice vectors have different magnitudes, as shown in Figure 4.6(a). Here the magnitudes of primitive vectors, namely the lattice constants in the reciprocal space, are not in scale with the ones in the real sample (where the inequality is much less), in order to increase the clarity of the schematic. Apart from the $\Gamma$-points inequality, all the branches follow the same dispersion behavior and polarization dependence as in the square lattice, as shown in the extinction spectra of a rectangular lattice with $p_x = 415$ nm and $p_y = 375$ nm.

### 4.3.4 45-Degree rotated square lattice

A square lattice with 45° rotation has the same symmetry as the normal square lattice, but neither of its primitive vectors are along the x- or y-axis, as shown in the schematic in Figure 4.7(a). The DOs are therefore dispersed and propagating differently: none of the lowest DOs are linearly dependent on the in-plane wave vector $k_y$; however they all can be supported both in TE- and TM-modes, because both $E_x$ and $E_y$ oriented dipoles have sufficient radiative component along the
SLRs on plasmonic nanoarrays with different lattice geometries

Figure 4.6. (a) The schematic of a rectangular lattice in reciprocal space and the four lowest DOs. Measured extinction and calculated DOs for (b) TE- and (c) TM-polarized light. Dashed and dotted white lines represent the DOs (0, 1) and (0, −1), respectively. The dashed red line represents the degenerate DOs (1, 0)/(−1, 0). Reproduced from Publication II with permission.

propagation directions of those DOs. See the measured extinction for a 45° rotated square lattice with the same particle separation as in Section 4.3.1 (375 nm) in Figures 4.7(b) and 4.7(c).

However, the second lowest order lattice vectors for a 45° square lattice are the same as the lowest orders for a normal square lattice, see the black dots lying on the x- and y-axes in Figure 4.7(a). Therefore the second-lowest order DOs become polarization dependent. Some features are found in the higher energy region of TE-mode measurement (Figure 4.7b) but not in TM-mode measurement (Figure 4.7c) since the supported degenerate DOs (1, −1)/(−1, 1) are not detectable in the defined wavelength range.

Figure 4.7. (a) The schematic of a 45° rotated square lattice in reciprocal space and the four lowest DOs. Measured extinction and calculated DOs for (b) TE- and (c) TM-polarized light. Dashed and dotted white lines represent the degenerate DOs (1, 0)/(0, 1) and (−1, 0)/(0, −1), respectively. Reproduced from Publication II with permission.
4.3.5 Honeycomb lattice

In the case of a non-Bravais lattice, as discussed in Section 4.1, the DO dispersions keep the same as in its corresponding Bravais lattice but the resonance will be modified by an *envelope factor*.

A honeycomb structure has a hexagonal Bravais lattice but with two particles within each unit cell, as shown in the schematic Figure 4.8(a). Take into account the particle locations in the unit cell, the *envelope factors* for the six lowest DOs are $1/2 + \frac{\sqrt{3}}{2}i$ for $(1, 0)$, $(0, 1)$, $(-1, -1)$ and $1/2 - \frac{\sqrt{3}}{2}i$ for $(1, 1)$, $(-1, 0)$, $(0, -1)$, respectively. Interestingly, the two factors both have unity magnitude, but with the opposite argument angles, meaning that the DOs from a honeycomb array have different phase shifts compared with the corresponding hexagonal array. But these phase shifts cannot be observed from extinction spectra.

![Figure 4.8](image)

**Figure 4.8.** The schematics of (a) a honeycomb lattice with its unit cells, which constitute a hexagonal lattice, and (b) a hexagonal lattice in reciprocal space and the six lowest DOs. Measured extinction and calculated DOs for (c) TE- and (d) TM-polarized light. Dashed and dotted white lines represent the DOs $(1,1)$ and $(-1,-1)$, respectively. Dashed and dotted red lines represent the degenerate DOs $(1,0)/(0,1)$ and $(0,-1)/(-1,0)$, respectively. Reproduced from Publication II with permission.

The measured extinction for a honeycomb array with a nearest particle separation of 250 nm and the calculated DOs for its corresponding Bravais hexagonal lattice are shown in Figures 4.8(c) and 4.8(d). The measurements still follow well with the DOs. However there is one pronounced difference from Figures 4.5(b) and 4.5(c), namely that the honeycomb array has a higher extinction. A honeycomb array has a higher filling fraction of metal particle therefore it also has a larger loss.

4.3.6 Lieb lattice

Following a similar procedure one can also consider the case of a Lieb lattice, which is composed by a square lattice with three particles within each unit cell, as shown in schematic Figure 4.9(a). The *envelope factors* from the three
SLRs on plasmonic nanoarrays with different lattice geometries

Figure 4.9. The schematics of (a) a Lieb lattice with its unit cells, which constitute a square lattice, and (b) a square lattice in reciprocal space and the four lowest DOs. Measured extinction and calculated DOs for (c) TE- and (d) TM-polarized light. Dashed and dotted white lines represent the DOs (0, 1) and (0, −1), respectively. The dashed red line represents the degenerate DOs (1, 0)/(−1, 0). Reproduced from Publication II with permission.

particles are all one.

The measured extinction of a Lieb array with a nearest particle separation 188 nm and the calculated lowest DOs for the corresponding Bravais square lattice are shown in Figures 4.9(c) and 4.9(d). The even higher (than in the honeycomb versus hexagonal) increase in the filling fraction of a Lieb lattice compared with square lattice results in less similarity between their measured spectra and broadens the linewidth of the SLR at the Γ-point for the Lieb lattice.

4.4 Numerical simulation

According to the measurement results, one can see that the supported SLRs of arrays with different geometries are mostly dependent on their DOs and the polarization directions, namely the detectable dipole orientations. So the far-field properties of a lattice structure (DOs) rule the coupling directions in which a near-field profile (dipole orientation) is oscillating in phase. In contrary, the radiative direction of the in-plane electric dipole determines whether or not a DO can be supported.

FDTD simulations for square arrays are performed as an example. The simulated extinction spectra with TE-polarized light under normal and 10° incident angles are shown in Figure 4.10(a). The simulated 0° incident resonance here corresponds to the measured spectrum Figure 4.4(b) at the Γ-point. And the 10° incident resonances correspond to the measured spectrum Figure 4.4(b) (0, 1) DO (for the peak at 553 nm) and (0, −1) DO (for the peak at 643 nm), respectively. The in-plane electric component phase profile, for TE-polarization being Φ(Eₓ), shows that the dipole oscillations on individual particles form a
standing wave, as indicated in Figure 4.10(b), because they are in phase. For 10° incident angle, as shown in Figure 4.10(c) and 4.10(d), the dipole oscillations form a phase front along the y-axis because they are not in phase but follow the propagation directions defined by DOs (0, 1) or (0, -1).

The same resonance wavelength is found in the simulated extinction spectrum of TM-polarized light under normal incident (at the Γ-point), but a different resonance wavelength under 10° incident angle, which corresponds to the measured spectrum Figure 4.4(c) the degenerate DOs (1, 0)/(−1, 0). The in-plane electric component phase profile shows that the dipole oscillations on individual particles form a standing wave the other way round as in the TE-polarized case, as indicated in Figure 4.10(f), still because they are in phase. For 10° incident angle, as shown in Figure 4.10(g), the dipole oscillations form a phase front along the x-axis because they are not in phase but follow a propagation direction defined by DOs (1, 0)/(−1, 0) and the in-plane wave vector \( k_y \).

![Figure 4.10](image-url)

**Figure 4.10.** FDTD simulated extinction spectra for square lattice under normal and 10° incident with (a) TE- and (e) TM-polarized light. The field distributions \( \Phi(E_x) \) for TE-polarized light at 583 nm wavelength under normal incidence (b), and under 10° incidence at 553 nm (c) and 643 nm (d) wavelengths. For TM-polarized light, the field distributions \( \Phi(E_y) \) at 583 nm wavelength under normal incidence (f) and under 10° incidence at 581 nm wavelength (g). Reproduced from Publication II with permission.

### 4.5 Conclusion

In this chapter, we have demonstrated experimentally the distinct SLRs supported by silver nanoparticle arrays of different geometries. The measured extinctions of square, hexagonal, rectangular, 45° rotated square, honeycomb and Lieb lattices show remarkably different SLR dispersions, though their Γ-points all have the same energy. And all the dispersions apart from those for the 45° rotated square lattice are found to be strongly dependent on the detection
polarization.

In order to interpret these features, we have proposed a simplified model where the radiative coupling between the LSPRs at individual particles follows the direction defined by the DOs of a lattice. In a non-Bravais lattice, each DO is modified by an envelope factor which is however not reflected in an extinction measurement. Under this framework the measured spectra show excellent agreement with the calculated DOs.

Furthermore, this model also reveals the principal propagation direction of each mode, along which the mode maintains its coherent properties. We have taken the case of the square lattice as an example. While the measured extinctions (Figures 4.4b and 4.4c) match exactly with the calculated DOs and the simulated spectra (Figures 4.10a and 4.10e), the simulations of the near-field distribution (Figures 4.10b-d, f, g) also reveal that at each resonance all the dipoles are oscillating coherently along the corresponding DO direction.
SLRs on plasmonic nanoarrays with different lattice geometries
5. **K-point lasing in a plasmonic honeycomb lattice**

In this chapter we go beyond the Γ-point and dig into the first Brillouin zone of plasmonic lattice. Specifically, based on the theoretical framework introduced in Chapter 4, we design and fabricate gold nanoparticle arrays with a honeycomb geometry and investigate their properties near the K-points of the first Brillouin zone. Measured with a higher numerical aperture (NA = 0.6) microscope objective, the extinction spectra of a plasmonic honeycomb lattice match well the calculated DOs in particular at the K-point. When immersing the array in a solution of dye molecules and pumping the sample with a femtosecond laser, we see clearly a lasing peak at the K-point position and prominent threshold curves. In a honeycomb lattice, the eigenstates at the K-point are two singlets and a degenerate doublet, all closely spaced in energy. In order to identify which one is the lasing mode observed in the experiments, we measure also the polarization dependence of the lasing emission, from which we can conclude that it is one of the singlets that is lasing in the experiments.

In Section 4.3.5, the SLR dispersions of a plasmonic honeycomb lattice have been presented, but only near the Γ-point. It will be interesting to investigate whether the theoretical framework is still suitable for describing the system for larger in-plane wave vectors \( k_\parallel \), for instance, at edges of the first Brillouin zone, namely, the K- and M-points, as shown in the schematic Figure 5.1a. From the Equation 4.3, it is quite straightforward to extend the honeycomb lattice DOs over the whole first Brillouin zone and along all the principal directions, Γ – M – K – Γ. The calculated DOs are shown in Figure 5.1b, where the curves with different colors indicate DOs with different orders – red for the 0\(^{th}\), fuchsia for the 1\(^{st}\) (which is referred as “lowest order” in the previous chapter), navy blue for the 2\(^{nd}\), purple for the 3\(^{rd}\) and green for the 4\(^{th}\).

Among these high symmetry points in the first Brillouin zone, K-points are worth a special focus as there might exist a Dirac point where two degenerate Bloch bands of the periodic potentials are crossing to form a gapless conical singularity, or at least some degenerate modes, which under suitable symmetry breaking could open a topological gap. Previous researches have studied K-points in radiatively coupled honeycomb or hexagonal lattice for photonic crystal lasing [83–86] and exciton-polariton condensation [87] systems. However, none
of these works showed convincing threshold phenomena, and the polarization properties of the output light were not analyzed. Here we demonstrate extremely high-quality lasing at the $K$-points, and show how the polarization properties and real-space patterns of the laser emission contain invaluable information about the lasing modes.

Figure 5.1. a. Schematic of the first Brillouin zone (green regions) of a honeycomb lattice and the high symmetry points; and b. the calculated DOs along the principal directions $\Gamma - M - K - \Gamma$.

5.1 Setup improvement and calibration for the $K$-point measurement

In order to observe the expected $K$-points in the experiments, the first step is to extend the detectable in-plane wave vector $k_\parallel$. Comparing Figures 4.8(b) and 5.1(a), the requirement is that $k_y$ (the blue arrow in Figure 4.8(b)) should be no less than the distance between the $\Gamma$- and $K$-points in the reciprocal space. Note that the orientation of the first Brillouin zone in Figure 5.1a is rotated by 90° compared with the reciprocal space Figure 4.8b, in order to collinearize the in-plane wave vector $k_y$ with respect to the direction of $\Gamma - K$.

The angles corresponding to the band edges at the $K$-point, namely the $K_0$, $K_1$ and $K_2$ points in Figure 5.1b, can be calculated (expressed as numerical aperture, $NA = n \sin \theta_{\text{max}}$ where $n$ is the refractive index of working medium, for comparing with the microscope objective specifications), taking into consideration the refractive index of the borosilicate substrate $n = 1.52$. The results are shown in Table 5.1.
Table 5.1. Angles corresponding to the first three band edges at the $K$-point in Figure 5.1b, in the form of numerical aperture $\text{NA} = n \sin \theta_{\text{max}}$. Each NA is firstly expressed as its dependence to the refractive index of the substrate, $n$, then the calculated value.

<table>
<thead>
<tr>
<th>Band edge position</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$K_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle (NA)</td>
<td>$n = 1.52$</td>
<td>$n/2 = 0.76$</td>
<td>$n/\sqrt{7} \approx 0.575$</td>
</tr>
</tbody>
</table>

The most suitable microscope objective for higher incident angles at the present has a numerical aperture $\text{NA} = 0.6$ (and magnification 40×). Therefore, only $K_2$ point at the band edge can be detected. The plasmonic honeycomb lattice in this chapter is designed and fabricated based on this assumption.

The second obstacle for measuring dispersion at the $K$-point is to overcome the optical distortion at higher angles. The angle-resolved spectrum setup, similar to the one introduced in the previous chapters, is used to guide the back focal plane of the microscope objective to the entrance slit of the spectrometer. The diffracted pattern through a grating inside the spectrometer is then focused on a 2D CCD camera of the spectrometer. Thus each pixel on the CCD image corresponds to a particular incident angle at a particular wavelength – the $x$-axis is used to resolve the wavelength and $y$-axis positions indicate the incident angles.

Since one has to collect large angles, an inevitable aberration occurs in the optical setup. This is because the image magnification is no longer uniform far from the optical axis. Normally in an image, the distortion is worse for the regions farther away from the center, as with the more severe distortion at wide-angle end in photography.

As an example we show the measured extinction spectrum of a square lattice with a periodicity $p_x = p_y = 575$ nm, see Figure 5.2. The measurement was done with $\text{NA} = 0.6$ microscope objective and the sample is placed in a $\theta_y \sim 10^\circ$ tilted stage in order to collect even larger angles. Comparison between the measured dispersion and the calculated DOs shows that while the position of the $\Gamma$-point still matches well, the $X$-point of square lattice deviates significantly. The measured band edge energy at the $X$-point is still close to the calculated result ($\sim 1.58$ eV), but the corresponding in-plane wave vector (and thus the angle) is much larger than expected. We reason that this apparent deviation may be due to optical distortion in the measurement setup.

In order to quantitatively adjust the measured spectra with the higher NA objective, a transmission grating with 300 grooves/mm is used to calibrate the optical distortion. Using the same detecting optics as the measurement setup, we measure the white light transmission spectrum, namely the diffracted pattern of the calibrating grating, see Figure 5.3a. Here the intensities are plotted on a $\log_{10}$ scale in order to increase the visibility of the higher diffracted orders. As explained before, the $y$-axis, along which the image has 400 pixels, corresponds to the incident angles at the slit of the spectrometer, and the $x$-axis corresponds to the wavelength.
The pixels where the diffracted orders reach their maximum intensity are then found at 10 nm intervals from 680 nm to 880 nm, as shown in Figure 5.3b. The actual diffracted angles at these wavelengths can be calculated:

\[ d \sin \theta_m = m \lambda, \]  

where \( d \) is the grating constant (1/300 mm) and \( m = 0, \pm 1, \pm 2 \) here as all the extracted spectra show five diffracted peaks.

The extracted peak pixels and the calculated angles (in the form of \( \tan \theta \) as it is related to magnification) are shown in Figure 5.3c. The deviation from a linear dependence indicates that there is, as expected, optical distortion. The zero incidence angle corresponds to the central pixel ~ 200. Clearly the magnification is decreasing with the distance from the optical axis, in line with the phenomenon of Barrel distortion. A Barrel distortion follows a quadratic function [88]. Therefore, the data points in Figure 5.3c are fitted with two quadratic functions for positive and negative angles (though they are almost identical). The measured spectra can be calibrated using these functions.
Figure 5.3. a. Diffracted pattern on the spectrometer CCD from a 300 grooves/mm transmission grating; b. the extracted pixels of the peak positions for every 10 nm (title of each panel indicates the wavelength); and c. their comparison with the calculated actual diffracted angles ($\tan \theta$) for these wavelengths.
Figure 5.4 shows the calibrated extinction spectrum for square lattice as in Figure 5.2, with the same measurement data. Clearly the match at higher angle is much better compared with non-calibrated spectrum. In particular, now the measured band edge at the $X$-point is very close to the calculated one in both energy and in-plane wave vector (angle) and is critical for the following measurement as it is also close to the expected position of band edge at the $K$-point of the current study.

![Calibrated extinction spectrum of a square lattice with a periodicity $p_x = p_y = 575$ nm and the calculated DOs. The match at higher angles is much better compared with Figure 5.2.](image)

**5.2 Dispersion of SLR in a honeycomb lattice**

According to the description in the previous section, honeycomb arrays of gold nanoparticle on borosilicate glass substrate are fabricated with diameter $d = 100$ nm, thickness $h = 50$ nm (still with 2 nm of titanium below as a adhesive layer) and the nearest particle separation varying between 569 – 583 nm, so that the $K_2$ points, as shown in the schematic in Figure 5.1b, are lying between 850 – 870 nm. The SEM image of the fabricated honeycomb array is shown as the inset of Figure 5.5.

To characterize the SLR dispersion, the high numerical aperture microscope objective is used as introduced above. The sample slide is placed on top of a
$\theta_y \sim 10^\circ$ tilted stage to collect some light from higher angles beyond the $K$-point. The array structure is immersed into a refractive index matching oil ($n = 1.52$) and a halogen lamp is used as the light source.

The measured data, calibrated with the above-obtained calibrating functions, gives the extinction spectrum of a honeycomb lattice array with the nearest particle separation $p = 576$ nm as shown in Figure 5.5. The dispersion matches perfectly with the calculated DOs, and comparing with Figure 5.1b, clearly the measured dispersion is a zoom-in of the full band diagram of a honeycomb lattice in the region near the highlighted $K_2$ point along the $\Gamma - K - M$ direction. This is also consistent with the schematic Figure 5.1a: that the measuring in-plane wave vector $k_y$ is along the $\Gamma - K$ direction, and pointing to the 2nd order $M$-point when going beyond the edge of the first Brillouin zone (with further increased angles).

![Figure 5.5. Calibrated extinction spectrum of a honeycomb lattice with a nearest particle separation $p = 576$ nm and the calculated DOs. The inset shows a SEM image of part of the sample, with the scale bar 500 nm. Reproduced from Publication IV.](image)

### 5.3 Lasing at the $K$-point in a honeycomb lattice

With the $K$-point observed in the dispersion, now it is time to try manipulating the mode population, e.g., to see if the SLR mode supported at the $K$-point(s) can be pumped to lase, like the nanolasers relying on the SLR $\Gamma$-point which have been studied experimentally in many previous works [28–32].
5.3.1 Feedback mechanism at the $K$-point

The optical resonator in a laser can be an arrangement of mirrors which supports a cavity mode [89]; or, as mentioned in Chapter 1, it can be implemented by the collective Bragg scattering from a periodic structure – the corresponding device is called a distributed feedback (DFB) laser [37, 90–93].

![Schematics for possible feedback mechanisms of the band edges at the a. $\Gamma$-, b. $M$-, and c. $K$-points.](image)

Plasmonic nanoparticle arrays, as one platform for DFB-type nanolasers, have been recently studied intensively [28–32], but all relying on the band-edge at the $\Gamma$-point, where two counter-propagating wave vectors encounter at the $\Gamma$-point, thus forming a standing wave, as shown in the Schematic Figure 5.6a (the previous works are mostly in square lattices, however the schematic shows the $\Gamma$-point of a hexagonal/honeycomb lattice – without loss of generality). At the $\Gamma$-point each nanoparticle has the same phase profile, and optical fields are localized at the dipolar hot spots; therefore, the feedback provides a directional control over the far field beam normal to the sample surface [41]. Physically this represents a 1D feedback. The 2D lasing at the $\Gamma$-point was also proposed and observed recently [94]. But the lasing action in that system was originated from correlation/coupling between sets of counter-propagating waves which cross at the $\Gamma$-point – different from the naturally 2D feedback at the $K$-point that will be explained in the following.

However, the other high-symmetry points of the Brillouin zone edges, which can also offer zero group velocities, have not been explored in plasmonic lattices so far. For instance at the $M$-point band edge of honeycomb or hexagonal lattice,
as shown in Figure 5.6b, the two counter-propagating wave vectors encounter not in the center of the Brillouin zone, resulting in an off-normal output beam, and the angle is dependent on the position of the corresponding $M$-point band edge. The $M$-point lasing has been observed in photonic crystals before [83] and can be achieved in a plasmonic lattice as well (our unpublished data).

The possible feedback condition for the band edge at the $K$-point can be more interesting, as there is no probable counter-propagating wave vectors encountering at the $K$-point. But rather, there can be three non-parallel wave vectors, as shown in the schematic Figure 5.6c, meeting at the $K$-point. Similar to the $M$-point, the feedback condition here cannot form a standing wave but a collective wavefront, therefore the output beam has an angle, dependent on the position of the corresponding $K$-point band edge. And unlike the band edges at the $\Gamma$- or $M$-points, here the feedback is purely 2D as it cannot be related to (a combination of) 1D DFB modes, but it is supported by a loop originating from the three non-parallel wave vectors, as shown in the inset of Figure 5.6c.

### 5.3.2 Lasing measurement

For the lasing measurement, the fabricated honeycomb lattice array is immersed into 25 mM concentration solution of IR-792 perchlorate dissolved into 1:2 (dimethyl sulfoxide)/(benzyl alcohol) solvent. Similar to the setup in Figure 3.2a, angle-resolved emission spectra are obtained with the higher numerical aperture microscope objective (NA = 0.6, ×40). The whole array together with the dye solution are pumped with a femtosecond laser with $\sim 60^\circ$ incident angle, 750 nm central wavelength, 100 fs pulse width and 1 kHz repetition frequency. The real and back focal plane images of lasing action are taken by focusing them to two separate 2D CCD cameras.

The pump power dependent emission properties of a honeycomb lattice with the nearest particle separation $p = 576$ nm is shown in Figure 5.7. Below the threshold, the emission spectrum only contains background noise signal. The emission intensity as a function of angle with several pump powers are shown in Figure 5.7(c). At the threshold pump fluence, an intense and narrow emission peak appears at $\sim 35^\circ$ with an angular divergence $\sim 0.8^\circ$ (the sub-features appearing at even larger angles for high pump fluence are likely due to the directional reading of the CCD pixels). The emission spectrum above the threshold, as shown in Figure 5.7(a), indicates the emission peak has a photon energy of 1.428 eV. Both the frequency and angle of the emission peak are perfectly in line with the position of the $K$-point band edge measured in the extinction spectrum as shown in Figure 5.5. The output power curve shows a rapid nonlinear increase of emission intensity (of more than three orders of magnitude) at the $K$-point angle, see Figure 5.7(b). Therefore, it is convincing that under this lattice configuration and pumping condition, the honeycomb array is lasing at the band edge at the $K$-point, with a remarkably increased output intensity and greatly decreased angular divergence.
To further characterize the $K$-point lasing, in particular to identify the lasing mode, more control experiments are performed. Especially the polarization dependence of the lasing mode is tested by taking both the Fourier and real space images of the lattice above threshold, which will be introduced in detail in the next section.

### 5.4 Polarization dependence of the $K$-point lasing

Generally, the properties of the eigenstates supported at the high-symmetry points are determined by group theory. As the reciprocal honeycomb lattice has $D_3$ point group symmetry around the $K$-points, as shown in Figure 5.1a, the $K$-point modes must constitute irreducible representations of the $D_3$ group. Using standard group-theoretical reduction methods [95], the electric dipole polarizations of the nanoparticles in the corresponding modes can be calculated. The irreducible representations of $D_3$ are either one- or two-dimensional, so the eigenstates are, apart from accidental degeneracies, either non-degenerate (“singlet”) or doubly degenerate (“doublets”). The $K$-point of the honeycomb lattice has a doublet and two singlets. For a more detailed symmetry discussion see Publication IV.

As the modes cannot be resolved from the extinction spectrum (Figure 5.5)
and one single lasing peak observed in the emission spectrum (Figure 5.7b), it becomes necessary to identify whether the measured lasing mode at the $K$-point is one of the singlets or the doublet.

5.4.1 Fourier images of the lasing action with different polarizations

A CCD camera is placed in the back focal plane to capture the Fourier image, i.e., the information from the reciprocal/k-space. To identify the lasing mode, the sample is pumped above the threshold power ($P = 1.2P_{th}$), and polarization dependent angle-resolved emission images are taken by the CCD camera and a linear polarizer at the detection path.

In the case of no polarizer, as shown in Figure 5.8a, all the six $K$-points in the first Brillouin zone are clearly visible at the edge of back focal plane. The faded features connecting some of the $K$-points (with smaller than one quarter of the intensities than at the lasing peaks) are due to the ASE of SLRs at other energies, as there is no band pass filter in the detection path. Figure 5.8b shows the angular distribution of emission intensity at each $K$-point. The angles of the polar axes indicate the polarizer angles and the radii refer to the normalized intensities. The emission intensities (the blue and olive green dots) behave as linearly polarized lights at all the lasing $K$-points, pointing from the corresponding $K$-point to the $\Gamma$-point. The measurements match perfectly with the calculated angular distributions of linearly polarized light having a polarization along the six $\Gamma$–$K$ directions, see the calculated red dashed lines. One of the singlet modes is found to have exactly the same properties, as shown in Figure 5.8c.
5.4.2 Real space images of lasing action with different polarizations

Another CCD camera, placed in the real focal plane, is used to further identify the lasing mode by taking real space images with different polarizer angles and comparing them with the theoretically calculated spatial intensity distributions.

Figure 5.9. Real space images of the lasing sample ($P = 1.2P_{th}$) a. without polarization filter; b. with horizontal polarizer; and c. with vertical polarizer. d – f. Theoretical simulations of the intensity distributions under the same configurations. Red and orange circles indicate the positions of nanoparticles; and arrows refer to the (projected) dipole polarizations (with respect to the polarizer direction) of the singlet mode for the zero $K$-$K'$ relative phase. Reproduced from Publication IV.

To calculate the spatial intensity distribution, the wave interference in the lattice is taken into account. Figure 5.9d shows the case of $K$- and $K'$-points lasing simultaneously with a fixed zero (modulo $\pi/3$) phase difference at the corresponding singlet mode (the mode represented by Figure 5.8c). Figures 5.9e and 5.9f show the projected intensity along horizontal and vertical polarization direction, respectively. They are consistent with the experimental real space images, as shown in Figures 5.9a-c. These further confirm that the system is lasing, as expected based on the polarization analysis of Figure 5.8, at the singlet mode, with comparable intensities and a fixed (or at least strong correlated) relative phase between the $K$- and $K'$-point lasing light.
5.5 Conclusion

In this chapter we have designed and fabricated honeycomb nanoparticle arrays, based on the theoretical framework introduced in Chapter 4, and shown lasing action at the $K$-points. For the first time a plasmonic lattice is found to lase at the edge of the first Brillouin zone, and both the angle and frequency of the lasing output are purely dependent on the lattice geometry. The lasing action is due to a naturally 2D feedback at the $K$-point of the honeycomb lattice.

To further identify the lasing mode, polarization dependent images have been taken both in Fourier space and in real space. The measured images consistently match the theoretical predictions for one of the singlet modes, with comparable intensity contributions from the $K$- and $K'$-points and a zero phase difference between them.

The characterization approaches introduced in this chapter are expected to be particularly fruitful in future studies related to topological photonics [96–99]. Radiatively coupled systems, especially the possibilities of supporting topologically non-trivial phenomena, have been investigated much less compared with the nearest-neighbor hopping systems. Here we have demonstrated lasing, and identification of the lasing mode by symmetry arguments and polarization analysis, in cylindrical nanoparticles of a honeycomb lattice. With proper choosing of, for instance, particle shapes or magnetic materials, one may anticipate an observable gap opening at the $K$-point which would open the way for studies of new phenomena, including topological ones.
$K$-point lasing in a plasmonic honeycomb lattice
6. Summary

In this dissertation, the properties of plasmonic nanoparticle arrays with different lattice geometries and their interactions with quantum emitters have been examined. Publication I and Chapter 2 of this dissertation presented a self-developed hybrid lithography-functionalization method for depositing silica-coated QDs on top of plasmonic nanorod arrays. The coupling between the QD emission and the SLRs supported by the plasmonic array induced an amplified directional light source. The high LDOS of SLRs especially at the $\Gamma$-point significantly enhanced the QD decay rate.

Publication III and Chapter 3 of this dissertation introduced briefly the observation of thermalization and condensation phenomena in a plasmonic lattice. Mapping the emission red-shift upon propagation, we quantitatively analyzed the interaction dynamics between SLR excitations and the surrounding dye molecules. The lattice geometry was found to have a direct impact over the measured emission spectra: a 30 nm change in periodicity realized a crossover from thermalization to BEC to lasing.

The final two chapters were the major part of this dissertation and discussed in detail the influence of lattice geometries on the SLR modes. The SLR dispersions with both TE and TM detection polarizations were systematically investigated on plasmonic arrays with different lattice geometries in Publication II. To interpret the measured dispersions, a generic theoretical framework was introduced, combining the collective DOs from the whole lattice and the dipole orientations on each individual nanoparticle. The theoretical framework was simple yet easy to be extended to the edge of the first Brillouin zone.

This framework was tested in Publication IV where a honeycomb nanoparticle array showed measured dispersion with perfect match to the calculated DOs also at larger angles, especially near the $K$-point. We were able to make the array lase at the band edge of the $K$-point, with a definite off-normal directionality ($\sim 35^\circ$). Since the $K$-point in reciprocal honeycomb lattice corresponds to the crossing of three DOs, the lasing action there has a naturally 2D feedback. In order to identify the lasing mode, we analyzed the polarization properties of the lasing action both experimentally and theoretically. We found that both the Fourier space images and the real space images show the same polarization
dependence as predicted for one of the singlet modes at the $K$-points.

The results of this dissertation, especially our finding of plasmonic $K$-points lasing, give a promising starting point to the study of topologically non-trivial phenomena in plasmonic lattices. We have investigated radiatively coupled systems, namely systems where the tight-binding model with (next)nearest-neighbor hopping \cite{100} is no longer a sufficient description, and shown auspicious results by manipulating merely the lattice geometries.

Though in this dissertation the plasmonic nanoparticle array already proved to be a fruitful platform for studies of many novel phenomena, there is still plenty to explore. The possibility of condensation at the $K$-point will be an interesting trial with the present setup and approaches. And as discussed in Section 5.5, a symmetry breaking mechanism that can open a sizable gap, for instance in for the degenerate doublet, may induce topologically protected modes. Furthermore, the polarization-resolved measurements that we introduced in Section 5.4 may be able to reflect more fundamental and crucial properties of a lattice, such as Berry curvature and quantum metric. Simplified effective models that can adequately approximate radiatively coupled lattice systems need to be developed as well, to aid the design of the systems and interpretation of results.
References


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