APPROVAL SHEET

Title of Dissertation: Discrete Metal-Semiconductor Nanoparticle Assemblies for Controlled Plasmon-Exciton Coupling

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NOTE: *The Approval Sheet with the original signature must accompany the thesis or dissertation. No terminal punctuation is to be used.

ABSTRACT

Title of Document: DISCRETE METAL-SEMICONDUCTOR NANOPARTICLE ASSEMBLIES FOR CONTROLLED PLASMON-EXCITON COUPLING

Haixu Leng, Ph.D., 2019

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One of the reasons why nanoscience is so fascinating is that the size of the nanosystems is "just about right". They are large enough to have various complex properties,

and at the same time they are small enough to be treated (calculated) by numerical methods. I studied the interaction between individual gold nanoparticles (in which plasmons are excited) and quantum dots (in which excitons are excited) experimentally and theoretically at the nanoscale. Coupling optical emitters (quantum dots) to plasmon resonances in metal nanostructures has long been investigated as a means to increase their spontaneous emission rates. This increased rate occurs for weak coupling between the emitter and plasmon; for intermediate coupling, a Fano resonance will be seen; under strong coupling, the system undergoes Rabi splitting into new, hybrid modes. To date, efforts at achieving strong coupling between plasmons and single emitters have mostly been studied in scattering measurements; however, Rabi splitting in the scattering spectrum is difficult to distinguish from the Fano interference, or induced transparency, that occurs at intermediate coupling strengths. Here, we report measurements of scattering and photoluminescence from individual coupled plasmonemitter systems that consist of a single quantum dot in the gap between a gold nanoparticle and a silver film. Splitting of the modes in photoluminescence is a signature of the strong coupling effect. The measurements unambiguously demonstrated weak, intermediate, and strong coupling at room temperature. In a separate study, we found that the photoluminescence of a quantum dot splits into two modes as a nanometer sized gold tip approaches the quantum dots on a gold substrate. The splitting in both cases was over 150 meV, which exceeded the plasmon cavity loss (definition of the strong coupling). These studies opened up the possibility of singlephoton nonlinearities and other extreme light-matter interactions at the nanoscale at room temperature.

DISCRETE METAL-SEMICONDUCTOR NANOPARTICLE ASSEMBLIES

FOR CONTROLLED PLASMON-EXCITON COUPLING

By

Haixu Leng.

Dissertation submitted to the Faculty of the Graduate School of the

University of Maryland, Baltimore County, in partial fulfillment

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doctorate of philosophy

2019

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2019

Dedication

This is dedicated to my girlfriend, Henan, for her support in the last 5 years. This is also dedicated to my family, specifically my mom, who always believes that I have the potential.

Acknowledgements

I joined UMBC physics department in Aug 2013. I am grateful that I was accepted to this great university. In 2014, I joined Dr. Pelton's group, and started my research. I want to thank Dr. Pelton, who always trusts the students' ability to achieve their goals. I spent two years to set up the home-made microscope. James Loy, the undergraduate student, made a LabVIEW program to control the motion stages. During the lab construction, Erik, our department lab specialist, helped me a lot in machining the optomechanical part. Dr. Takacs taught me how to use the electron microscope. I want to thank them for their help.

I also want to thank Brian Szychowski and Dr. Daniel for their amazing work in synthesizing the samples.

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[Melnikau, D J. Phys. Chem. Lett. 2016. 7 (2). 354–362] Copyright 2018 American Chemical Society.
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Chapter 1: Introduction

1.1 Overview

On Dec 29th 1959, Nobel laureate Richard Feynman gave a speech at the annual American Physical Society meeting, "There's plenty of room at the bottom," predicting the emergence of a new field, nanoscience. In nanoscience, we study the physics of objects on the nanometer scale (10^{-9} m) , which is often very different compared to macroscale physics. Serious efforts have been made in studying the optical properties of isolated nanoparticles, including semiconductor nanoparticles¹ and metal nanoparticles.² Recently, there has also been much interest in the interaction between semiconductor nanoparticles and metal nanoparticles.³ New optical properties can be seen when the interaction between a semiconductor nanoparticle and a metal nanoparticle is strong. It was theoretically proposed that these new optical properties from the interaction between nanoparticles can be controlled by exciting the nanoparticles with a laser.⁴ In my thesis, I studied the interaction between a semiconductor nanoparticle and the gap plasmon that was formed by metal nanoparticles and metal films. This research laid the groundwork for development of nanoparticle assemblies as a key enabling technology for future optical information processing at high speeds and low powers, including quantum-mechanical information processing at the single-photon level.⁵

In Dr. Pelton's lab, I made measurements to study the interaction between a quantum dot (QD) and gap plasmons. The QDs that we used were cadmium chalcogenide nanocrystals (or II-VI compounds), which were chemically synthesized

in organic solvent by our collaborators from Dr. Daniel's group (UMBC chemistry). In addition, a shell of high band gap material (CdS) were grown on the CdSe core to improve the photoluminescence quantum yield. The quantum yield in photoluminescence is defined as number of photons emitted divided by the number of photons absorbed. A photo of QDs in solution can be seen in Figure 1a. The emission wavelength of a QD can be tuned during synthesis. These features make the QD a perfect candidate for single-emitter strong coupling studies.

A plasmon is a collective oscillation of conduction band electrons.^{6,7} The gap plasmon is a type of plasmon that is formed by a gold nanoparticle (GNP) with a metal film (gold or silver). In the small gap between the GNP and the metal film, the electric field is extremely intense. A plot of the calculated electric field distribution for a gap plasmon can be seen in Figure 1b. In order to achieve strong coupling between a QD and gap plasmons, my collaborators and I used several methods to put the QD in this gap. This strong electric field generated by the gap plasmon can work as a bridge that couples the QD with the gap plasmon.



Figure 1 a. Luminescence from solutions of QDs with different emission wavelengths. The emission wavelengths of the QDs can be controlled by varying their size. Photo from Dr. Pelton. **b**. An illustration

of a QD (red spot) located in the gap between a 100 nm GNP and a silver film. The intensity of the electric field (E_y , polarized vertical to the silver film) is shown in a thermal color map. The electric field tends to concentrate near the gap area. The simulation was done in COMSOL Multiphysics software.

In the system consisting of a QD and gap plasmon, the optical property is unique and controllable. An example is shown in Figure 2. In this example, from Ref. 4, the scattering/extinction spectra of a coupled system was calculated. This coupled system consists of a QD and two silver ellipsoids. The QD sits in the gap between the two ellipsoids. Without the QD, the extinction spectrum had a Lorentzian shape (green circles). With the QD, the extinction spectra had a dip in the spectrum (black squares). In another study, it was predicted that this dip can be controlled by a laser. Under continuous laser illumination, the electron inside the QD will be kept in the excited state, and the QD thus can no longer interact with the plasmonic cavity.³ In other words, the saturated QD is decoupled from the gap plasmon. As a result, the extinction spectrum of the system will shift from the curve shown by the squares to the curve shown by the circles. However, the configuration shown in Figure 2 is difficult to realize in experiments. During my PhD research, I used gap plasmons formed by a GNP and a silver film to test the predictions in Ref. 4. In another study with our collaborators, a gold tip was used to form the gap plasmon with a gold film.



Figure 2 Calculated scattering spectrum for a system consisting of a single semiconductor nanocrystal (QD) between a pair of ellipsoidal silver nanoparticles. The squares and circles are generated from a finite-difference time-domain simulation, and the solid line is a fit to a phenomenological coupled-oscillator model. The squares and the line show the spectrum with the semiconductor nanocrystal, and the circles show the spectrum without the nanocrystal (QD). The linewidth/loss of the QD γ_{QD} was set as 10 meV. Reprinted with permission from ref⁴, © 2010 Optical Society of America.

1.2 Theory

1.2.1 Overview of the theory involved

My thesis study was a follow-up study of a theory paper published by Dr. Wu, Dr. Gray and Dr. Pelton in 2010.⁴ In this theory paper, Dr. Wu proposed a structure consisting of two aligned silver nano-ellipsoids and a QD in the gap. The QD is a small semiconductor nanocrystal; commonly used QDs are synthesized in organic solvent and have diameter less than 10 nm. Two different calculation approaches were used in this paper, including a classical coupled oscillator model and a finite-difference timedomain simulation (FDTD). In the FDTD simulation, the scattering spectra of the structure (two Ag ellipsoids and a QD) were simulated.

From the FDTD simulation, Dr. Wu found that the scattering spectrum of the structure had a dip, which was very different from the scattering spectrum of just two Ag ellipsoids without the QD. Intuitively, one might expect that the small QD should not change the scattering of two silver ellipsoids. Dr. Wu argued that, when a QD is placed in the right location (gap), it can introduce a Fano dip in the scattering of the silver ellipsoids if the QD resonance energy matches the plasmonic resonance of the Ag ellipsoids. This Fano dip is a result of an interference between the QD resonance and the plasmon resonance of the two ellipsoids, which will be discussed in detail later in section 1.2.5. The calculated Fano dip is shown in Figure 2. Dr. Wu also showed that a classical coupled oscillator model can generate very similar results as the FDTD simulation.

Later, Dr. Shah from Dr. Gray's group further investigated this topic in 2013.⁸ Dr. Shah found that the results Dr. Wu reported in 2010 were not limited to the specific models used in the calculation. The same results (a dip in the absorption/scattering spectra) were found using a discrete dipole approximation (DDA), a cavity-quantum-electrodynamics (CQED) and a semi-classical (SC) model. The result is shown in Figure 3. Further, it was shown in calculations that the dip would disappear under continuous-wave laser pumping. This result provided a way to actively control the optical property of this nano-structure (shown in the insert of Figure 3) using a laser.

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Figure 3 Linear absorption spectrum of a Au-CdSe-Au hybrid nanoparticle system (illustrated in the inset). Absorption spectra, σ_{abs} , are calculated using the discrete dipole approximation (DDA), cavity-quantum-electrodynamics (CQED) and semi-classical (SC) models. Figure from Dr. Shah's paper.⁸

Other than the Fano dip, there are also theoretical studies showing that the spectra in scattering or photoluminescence (PL) measurements will split into two modes (two peaks in spectra) if the coupling strength is strong enough.^{4,9–11} Based on the definition of strong coupling, the splitting needs to be larger than the spectral linewidth (loss) of both the QD and the optical cavity. In a scattering measurement, a Fano dip can be easily confused with the splitting (two peaks) in strong coupling, because they look alike. In order to experimentally demonstrate a strong coupling effect we need to take photoluminescence measurements. Scattering is a coherent process, so the Fano interference can introduce a dip in the scattering spectrum. However, it does not introduce a dip in the photoluminescence spectrum, because photoluminescence is

an incoherent process. As I found in the experiment, for a structure showing a Fano dip in the scattering spectra, the photoluminescence measurement did not show any dip at all.

In summary, numerous theoretical papers have predicted that a Fano dip can be observed in the scattering from a coupled system consisting of a QD in the gap between two metal nanoparticles. At a higher coupling strength, a splitting was predicted.¹¹ This strong coupling splitting needs to be further confirmed by a splitting in photoluminescence measurements. In my thesis, I tested these predictions in the lab.

I will introduce the theory of QDs and plasmons first. Then, I will discuss the theory of weak coupling, Fano resonance (intermediate coupling), and strong coupling. At the end of this section, a short discussion of the importance of single-emitter coupling will be given. More technical details of QDs and gap plasmons can be found in section 2.2.

1.2.2 Quantum dots

To understand the physics of a QD, the QD can be approximated as an electron confined in a small box, where the electron can move around within the QD freely but cannot move outside of the box, as shown in Figure 4.



Figure 4 Electron confined in a three-dimensional box.

Inside the box of Figure 4, the potential $V_{in} = 0$, and $V_{out} = \infty$ outside of the box. Applying the Schrodinger equation to this simplified model, within the box we get:

$$-\frac{\hbar^2}{2m^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(\mathbf{x}, \mathbf{y}, \mathbf{z}) = E_{x, y, z} \psi(\mathbf{x}, \mathbf{y}, \mathbf{z})$$
(1)

where $\psi(x, y, z)$ is the wave function, $E_{x,y,z}$ is the energy, and m^* is the effective mass of the electron in the box. By the method of separation of variables, we can write $\psi(x, y, z) = \varphi(x)\varphi(y)\varphi(z), E_{x,y,z} = E_x + E_y + E_z$. Now, substituting these equalities into Eq (1), in the x direction,

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2}{\partial x^2}\varphi(\mathbf{x}) = E_x\varphi(\mathbf{x})$$
(2)

$$\varphi(\mathbf{x}) = A\sin(k_x x) + B\cos(k_x x) \tag{3}$$

where $k_x^2 = \frac{2m^* E_x}{\hbar^2}$. If we set the origin at one of the corners of the cube and the electron cannot move out of the box, then

$$\varphi(0) = 0 \tag{4}$$

We find that B must equal to 0, then at $x = L_x$, $\varphi(L_x) = 0$. We thus get

$$k_x L_x = n_x \pi \tag{5}$$

where n_x is an integer. Since $(k_x L_x)^2 = \frac{2m^* E_x}{\hbar^2} L_x^2 = (n_x \pi)^2$, $E_x = \frac{\hbar^2 n_x^2 \pi^2}{2m^* L_x^2}$. Thus, in the end we get

$$E_{x,y,z} = \frac{\hbar^2 \pi^2}{2m^*} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$
(6)

From this result, we can see that the states in the box are discrete and inversely proportional to L^2 . This feature can be considered as the quantum confinement effect: small QDs (smaller *L*) will lead to a blue color in emission (larger *E*), while large QDs will have a red color. In the real world, QDs have various shapes (different L's) and compositions (different *m*^{*}), and more sophisticated theoretical models need to be used to calculate the band structure of the QD.

A TEM image of the CdSe/CdS core/shell QDs we used is shown in Figure 5. Generally, chemists can tune the optical property of a QD by varying the size (L) of it.



Figure 5 TEM image of the CdSe/CdS QDs. TEM image was taken by Dmitriy Dolzhnikov from Northwestern University.

In my thesis, I chose a QD as the emitter other than organic dye molecules because of its large dipole moment. Moreover, intense research has been done on QDs in the last decade,¹² which makes QDs perfect emitters in my study.

1.2.3 Plasmons

On a metal surface, electron waves propagate along the surface, coupled to oscillating electric fields outside of this surface, and this coupled electron-electromagnetic wave on a metal surface is a surface plasmon. If we further confine this surface plasmon by considering a metal nanoparticle, in this case, we can think of a metal nanoparticle as a rolled-up surface. By analogy, because of this "rolled-up surface", standing surfaceplasmon waves will be formed, which have specific modes with strong resonances. The surface plasmon within a metal nanoparticle is called a "localized surface plasmon". An illustration of localized surface plasmons is shown in Figure 6.

In my study, emitters were coupled to plasmonic cavities. These plasmonic cavities were formed by gold nanoparticles and a metal film. In these cavities, a strong localized electromagnetic near-field can be generated due to the distribution of charges during the electron oscillation. This strong near-field is critical for the coupling between the cavity and an emitter, because the emitter can be considered as a dipole, and a dipole interacts with electromagnetic fields.



Figure 6 An illustration of a localized surface plasmon in a metal nanoparticle. Under the excitation, conduction electrons within a metal nanoparticle oscillate collectively in response to the driving field. Strong near-field can be produced near the metal nanoparticle because of the localized charges. Figure from ref.¹³

In order to understand the physics of a localized surface plasmon, I will use a small gold nanoparticle (GNP) as an example. A typical GNP is much smaller than the wavelength of the excitation fields; as a result, we can assume the GNP is immersed in a uniform field. This assumption is the quasistatic approximation. According to electromagnetic theory, potentials inside and outside of the GNP can be described in terms of Legendre polynomials:⁷

In order to calculate the scattering spectra of a GNP, we can calculate the potential within the spherical gold particle (r < a, where *a* is the radius of the particle):

$$\phi_{in}(r,\theta) = \sum_{l=1}^{\infty} A_l r^l P_l(\cos(\theta))$$
(7)

Outside of the particle $(r \ge a)$, the potential can be described as

$$\phi_{out}(r,\theta) = \sum_{l=1}^{\infty} B_l r^{-(l+1)} P_l(\cos(\theta)) - Ercos(\theta)$$
(8)

where $P_l(\cos(\theta))$ are the Legendre polynomials. Within the particle, we only have the r^l term because r is finite. Outside of the particle we only have the $r^{-(l+1)}$ term because r cannot be zero. $-Ercos(\theta)$ is the background potential, if we define field to be in the Z direction. Then, we apply the boundary condition that the potential and the normal component of the electric displacement D are continuous at r=a. Under the quasistatic approximation, only the l=1 case exists, which is the dipole term. This simplification was first used in Mie theory, in which the scattering of small dielectric particles were calculated.¹⁴ As a result, we have:

$$\phi_{out} = -E_0 r \cos\theta + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_0 a^3 \frac{\cos\theta}{r^2}$$
(9)

where ϵ_m is the dielectric function of the medium and ϵ is the dielectric function of the particle (gold, in this case). This can be rewritten as the potential of a dipole,

$$\phi_{out} = -E_0 r \cos\theta + \frac{\mathbf{p} \cdot \mathbf{r}}{4\pi\epsilon_0 \epsilon_m r^3} \tag{10}$$

where p is the dipole moment of the particle, which can be calculated from Eq (9) and Eq (10):

$$p = 4\pi\epsilon_0\epsilon_m a^3 E_0 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \tag{11}$$

Note that ϵ is frequency dependent. We can thus see from Eq (11) that, when the denominator $\epsilon + 2\epsilon_m$ reaches its minimum, the system exhibits a resonance, corresponding to the plasmon resonance. For the gold/air interface, $\epsilon_m = 1$, so $\epsilon_{real}(\lambda)$ should be -2 at resonance. This corresponds to a resonance wavelength at around 500 nm for gold.⁷

The electric field does not only depend on the dipole moment, but also depends strongly on the distance r. This means that the electric field is strongly confined to the region near the surface of nanoparticles. The electric field outside of the sphere (r>a) of the dipole can be found as:

$$\boldsymbol{E} = -\nabla \boldsymbol{\phi} = \frac{1}{4\pi\epsilon_0} \left(\frac{3(\boldsymbol{p} \cdot \hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \boldsymbol{p}}{r^3} \right)$$
(12)

where *p* is the dipole moment, and \hat{r} is the unit vector of the field. Along the sample direction of the dipole, this field can be found as:

$$\boldsymbol{E}_{\boldsymbol{p}} = \frac{1}{4\pi\epsilon_0} \left(\frac{2p}{r^3}\right) \tag{13}$$

From this equation, we can see a dependence of E on r^{-3} along the direction of the dipole. An illustration of this field confinement can be found in Figure 7.



NP diameter 60 nm

Figure 7 Calculated near field distribution of a 60 nm GNP, which is normalized by the incident field E_0 , which is polarized along the horizontal direction. The field enhancement of E/E_0 is plotted. Image from <u>nanoplasmon.com</u>.

The scattering coefficient can be calculated, which is proportional to the square of p:¹⁵

$$C_{scatt} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right|^2 \tag{14}$$

Note that this formula has a very important implication in scattering measurements: because of the a^6 dependence, small nanoparticles (less than 40 nm) are difficult to detect in a scattering measurement.

1.2.3.1 Gap plasmons

In practice, I used gap plasmons to further increase the local intensity of the electromagnetic field. In the case of two GNPs, the plasmons interact due to Coulomb forces between charges on the surfaces of each of the nanoparticles. Across the gap,

these Coulomb forces are strong, leading to a large redistribution of the charges. The smaller the gap, the more the charges interact and localize, leading to a greater localization of the field within the gap. If the separation d between the two GNPs is much smaller than the radius of the GNP, then the field inside the separation/gap is proportional to d^{-3} . This strong field in the gap is often referred to a "hot spot", which is used to enhance the signal in Raman scattering for molecular sensing applications.¹⁶ An illustration of the "hot spot" is shown in Figure 8.



Figure 8 The calculated map is showing the electric field distribution around gold nanoparticle dimmer. Particle diameter is 20 nm, interparticle separation is 2 nm, and the incident field is polarized in the xdirection. The wavelength of the incoming light is 534 nm. Image from http://www.silmeco.com/knowledge-base/hot-spots/h

Instead of using a gap plasmon formed by two GNPs, a gap plasmon formed by only one GNP and its image inside of a nearby metal film was implemented. The induced image by a GNP inside the metal film interacts with the original GNP to produce a gap plasmon. In this gap plasmon setup, a GNP was deposited on a metal film to form a gap, as shown in Figure 9. It was found in numerical simulations and experiments that, as the separation (gap) between the GNP and the metal film is reduced, the electromagnetic field in the gap increases.¹⁷ This occurs because, as the separation decreases, the GNP and its image get closer, and a higher charge density accumulate across the gap, leading to a higher electromagnetic field. The field enhancement $(|E|^2/|E_0|^2)$ in the gap can be as high as 10³, depending on the geometry of the structure.



Figure 9 a An illustration of a gap plasmon setup, where a GNP is placed on a metal film. The GNP interacts with its image to create a strong electromagnetic field inside the gap. **b** Distribution of electromagnetic fields with various separation size between the GNP and the metal film, calculated using a full-wave numerical simulations. Image from Professor David R. Smith's web page.

In general, the plasmon resonance and the field localization of the gap plasmon depend on (1) the separation between the film and the GNP, (2) the size of the GNP, (3) the dielectric constant of the spacer film, and (4) the shape of the GNP.¹⁸

1. The gap plasmon resonance redshifts as the separation becomes smaller. This phenomenon can be explained by a dipolar model, which is shown in Figure 10.
In this model, the plasmon resonance is determined by the restoring (Coulomb) force between the positive charge and the negatively charged electrons. When the GNP dipole interacts with its image inside the metal film, opposite-sign charges will accumulate across the gap, as shown in Figure 10 (b). The attractive Coulomb force between the opposite charges across the gap reduces the restoring force within each individual particle, which leads to a lower resonance frequency.¹⁹ The plasmon resonance is analogous to a spring: the less stiff the spring, the lower the resonance frequency. This red-shift can be validated in a numeric simulation, as shown in Figure 11. In this example, the scattering of a 100 nm GNP on a gold film was simulated and the plasmon resonance is seen to red-shift from 560 nm (GNP alone) to around 700 nm as the gap changes from 50 nm to 1 nm. The separation between a GNP and metal film can be easily controlled by depositing a dielectric spacer with a specific thickness on the metal film. This dielectric spacer can be grown by sputtering or atomic layer deposition (ALD).

2. In a similar way as case 1, if we increase the size of the GNP on a metal film while keeping the separation distance constant, then the relative gap size compared to the case with a smaller GNP decreases. This decrease in the relative gap separation redshifts the plasmon resonance. The size of the GNP can be controlled in synthesis. Because of the fact that only GNPs larger than 50 nm can be seen in our single-particle scattering measurements, I used GNPs with diameters of 100 nm in diameter for a good signal to noise ratio. For GNPs

larger than 100 nm, the quadrupole mode starts to dominate the plasmon resonance.²⁰



Figure 10 Sketch to illustrate the electromagnetic interaction between closely spaced nanoparticles, (a) an isolated particle, (b) a pair of close particles with the polarization of the exciting field parallel to the long particle pair axis and (c) orthogonal to the long particle pair axis. Reprinted with permission from ref,¹⁹ Copyright © 2003 Elsevier Science.



Figure 11 Calculated plasmon resonance of the gap plasmon formed by a GNP (100 nm in diameter) and a golden film. The separation between the bottom of the GNP and the film surface varies from 50 nm to 1 nm (left to right). The FEM calculation was done in the COMSOL Multiphysics software.

3. A higher dielectric constant of the spacer in the medium will result in a greater screening effect, which will weaken the restoring force between the charges. This weakened restoring force will lead to a lower resonance frequency (a redshift). The dielectric constant of the medium can be controlled by changing the material of the spacer. For instance, the GNP on the metal film can be coated with a high dielectric constant material to redshift the plasmon resonance.²¹

4. The geometry of the GNP near the gap is also important, as shown by Dr. Baumberg's group in a paper studying the gap plasmon resonance frequency when varying the shape of the GNP. ²² Specifically, a flat surface of the GNP (instead of a round surface) will redshift the plasmon resonance. A measurement of several GNPs on an Ag film is shown in Figure 12, where the scattering spectra differ from particle to particle due to the heterogeneous sample population.



Figure 12 Scattering spectra of several gap plasmons, formed by 100 nm GNPs on a silver film. The variances in the scattering spectra were results of the heterogeneities in the GNP sample. GNPs with different shape and size will have different gap plasmon when coupled to a silver film. The insert shows the strong field in the gap in simulation.⁵

1.2.4 Enhanced spontaneous emission in weak coupling

In the weak-coupling regime, the emission rate of an emitter can be enhanced by the presence of a strong electric field. This enhancement can be understood in a similar

way as stimulated emission and absorption. In stimulated emission, an emitter in the excited state will be driven to its ground state, if the energy between the excited state and the ground state is in resonance with the driving field ($\hbar\omega$). On the other hand, spontaneous emission can be considered as stimulated emission that is stimulated by a vacuum field. A plasmonic metal nanoparticle enhances this vacuum field the same way it enhances real fields, resulting in an enhanced spontaneous-emission rate.

In the weak-coupling regime, the emission rate of an emitter in an electric field can be described by Fermi's golden rule:²³

$$\Gamma = \frac{2\pi}{\hbar^2} \langle g | \boldsymbol{\mu} \cdot \boldsymbol{E} | \boldsymbol{e}_1 \rangle \rho(\omega) \tag{15}$$

where $\langle g |$ is the ground state of the emitter, $|e_1\rangle$ is the excited state of the emitter, μ is the dipole matrix element, E is the electric field, and $\rho(\omega)$ is the local density of states. When the emitter is weakly coupled to a metal nanoparticle (a plasmonic cavity), the decay rate of the emitter increases because $\rho(\omega)$ will be larger compared to a standalone emitter.

1.2.5 Fano resonance in intermediate coupling



Figure 13 Schematics for understanding modified emission due to metal nanostructures: (1) radiative decay at rate Γ_0 ' from the emitter into free space; (2) non-radiative decay by the emitter at rate Γ_{nr}^{em} ; (3) quenching of the emitter by the metal at rate Γ_q ; (4) decay of the emitter by exciting plasmons in the metal nanostructure at rate Γ_g ; (5) radiative decay of plasmons at rate Γ_r^{pl} ; (6) non-radiative decay of plasmons at rate Γ_{nr}^{pl} . Figure from ref²³.

In the weak-coupling regime, energy will be transferred from an emitter to a plasmon cavity with a rate much smaller than the energy dissipation rate in the plasmon cavity. This relation can be described as $\Gamma_g << \Gamma_{pl}$, and $\Gamma_{pl} = \Gamma_r^{pl} + \Gamma_{nr}^{pl}$. An illustration is shown in Figure 13, where Γ_g is the coupling rate between the emitter and the plasmon cavity and Γ_{pl} is the energy dissipation rate of the plasmon, including the radiative decay rate Γ_r^{pl} and the non-radiative decay rate Γ_{nr}^{pl} . On the other hand, if the energy transfer rate between the emitter and the plasmon Γ_g is much larger than the plasmon dissipation rate Γ_{pl} , the emitter can be re-excited by the plasmon; then the emitter and the plasmon are in the "strong-coupling" regime.⁷ Between "strong coupling" and "weak coupling", there is an intermediate regime, in which novel phenomena can still occur.

The interaction between an emitter and the plasmon can be modeled as two coupled harmonic oscillators. This model was used by Dr. Wu in his paper,⁴ where he studied the interaction between a QD and a plasmon cavity formed by two silver nano-ellipsoids, as shown in Figure 2.

In the coupled-oscillator model, displacements of electrons inside of the QD (x_{QD}) and the plasmon (x_{SP}) are driven by external fields:

$$\frac{\partial^2}{\partial t^2} x_{SP} + \gamma_{SP} \frac{\partial}{\partial t} x_{SP} + \omega_{SP}^2 x_{SP} + g \frac{\partial}{\partial t} x_{QD} = F_{SP}$$
(16)

$$\frac{\partial^2}{\partial t^2} x_{QD} + \gamma_{QD} \frac{\partial}{\partial t} x_{QD} + \omega_{QD}^2 x_{QD} - g \frac{\partial}{\partial t} x_{SP} = F_{QD}$$
(17)

where $\omega_{SP} (\omega_{QD})$ is the plasmon (QD) resonance frequency, $\gamma_{SP} (\gamma_{QD})$ is the plasmon (QD) decay rate, and g is the coupling constant. F_{SP} and F_{QD} are the driving forces for the plasmon and the QD; because of the small size of the QD, we can assume $F_{QD} = 0$. Then, F_{SP} drives the two oscillators with a frequency ω , and $F_{SP}(t) = F_{SP} e^{-i\omega t}$. Both the QD and the plasmon follow this driving force at the same frequency ω , so we have $x_{QD}(t) = x_{QD} e^{-i\omega t}$ and $x_{SP}(t) = x_{SP} e^{-i\omega t}$. If we plug these harmonic terms back into Eq (16) and Eq (17), we can get

$$x_{SP}(t) = Re\left(\frac{(\omega_{QD}^2 - \omega^2 - i\gamma_{QD}\omega)F_{SP}(t)}{(\omega^2 - \omega_{QD}^2 + i\gamma_{QD}\omega)(\omega^2 - \omega_{SP}^2 + i\gamma_{SP}\omega) - \omega^2 g^2}\right)$$
(18)

$$x_{QD}(t) = Re\left(\frac{-ig\omega F_{SP}(t)}{\left(\omega^2 - \omega_{QD}^2 + i\gamma_{QD}\omega\right)\left(\omega^2 - \omega_{SP}^2 + i\gamma_{SP}\omega\right) - \omega^2 g^2}\right)$$
(19)

In this case, the surface plasmon (SP) and the QD are coupled through the first order time derivative term of *x*. The scattering intensity of the structure can be described as *S*, and $S \propto |\alpha|^2$, where α is the polarizability of the nanostructure. Using $\alpha \propto F_{SP} x_{SP}$, we get:⁴

$$S(\omega) \propto \omega^4 \left| \frac{(\omega_{\rm QD}^2 - \omega^2 - i\gamma_{\rm QD}\omega)}{(\omega^2 - \omega_{\rm SP}^2 + i\gamma_{\rm SP}\omega)(\omega^2 - \omega_{\rm QD}^2 + i\gamma_{\rm QD}\omega) - \omega^2 g^2} \right|^2$$
(20)

In Dr. Wu's paper,⁴ the scattering spectrum of a system consisting of a QD and two silver ellipsoids was simulated using FDTD, and the result is shown in Figure 2. In this scattering spectrum, a dip was found at the energy of the QD resonance. This simulation can also be reproduced using Eq (20), shown as the red curve in Figure 2. This dip is understood as a result of a Fano inerference between a narrow-linewidth resonance (emitter) and a broad-linewidth resonance (plasmon). The Fano resonance was first discovered by Ugo Fano in a study of asymmetric peaks in the excitation spectrum of He.²⁴ In Fano resonance, two resonances (one with a narrow linewidth and one with a broad linewidth) are excited, and the total response of the system is the superposition of the two resonances. Consequently, asymmetric spectra are created with a dip.

In our study, the scattering spectra of nanoparticles were measured first, then I fitted the data using Eq (20), which gave the coupling strength g. In the end, I compared this coupling strength g with the linewidth of the plasmonic cavity; if g exceeded the linewidth of the plasmonic cavity, then this specific system was in the strong-coupling regime by definition. In Eq (20) and elsewhere in my thesis, g is equal to the vacuum

Rabi frequency, which differs by a factor of 2 from the definition of g used in some cases in the literature.¹⁰

This coupled-oscillator model effectively treats the QD as a two-level system, ignoring the details of its energy-level structure and spatial variations in its coupling to electric fields. It also ignores any frequency dependence of the dielectric function of the metal across the plasmon resonance, which is an adequate approximation for photon energies far from the energies of interband transitions in the metal.

The spectrum for a Fano resonance looks very similar to the two-peak spectrum for strong coupling. It is also known that the irregular structures in a gap-plasmon setup can induce a two-peak feature in the scattering measurements even in the absence of any coupling to an emitter.¹⁸ In this case, it is critical to use incoherent methods, like photoluminescence, to determine whether strong coupling has been achieved.

1.2.6 Strong coupling

A quantum-mechanical description of the strong coupling regime was first developed for a system that involves micro-cavities.^{25,26} In our case, we used a plasmonic cavity instead, which can be considered as a micro-cavity with a smaller mode volume and higher loss rate.

First, let us consider a simple picture. If we ignore the damping or the decay terms, then the interaction can be determined by the Jaynes-Cummings Hamiltonian:

$$H_{JC} = \frac{1}{2}\hbar\omega_0\sigma_z + \hbar\omega a^+ a + \frac{g}{2}(a\sigma^+ + a^+\sigma^-)$$
(21)

where ω_0 is the transition frequency, σ_z is the Pauli spin operator, ω is the cavity resonance frequency, *a* is the cavity lowering state operator, *g* is the coupling strength

and σ^- is the atomic state lowering operator. In this case, two states are coupled, |n, e >and |n + 1, g >. In |n, e >, there are *n* photons in the cavity and the atom (emitter) is in the excited state. In |n + 1, g > there are n + 1 photons in the cavity and the atom is in the ground state. By solving the Jaynes-Cummings model, two eigenvalues are found:

$$E_{+} = \hbar \left(n + \frac{1}{2} \right) \omega + \hbar \frac{g}{2} \sqrt{n+1}$$
(22)

$$E_{-} = \hbar \left(n + \frac{1}{2} \right) \omega - \hbar \frac{g}{2} \sqrt{n+1}$$
(23)

The general solution can be written as a superposition of these two eigenstates:

$$|\Psi(t)\rangle = c_{en}(t)|n, e\rangle + c_{gn+1}(t)|n+1, g\rangle$$
(24)

If we set the original state as |n + 1, g >, the time evolution of the coefficient can be found as

$$|c_{en}(t)|^2 = \cos^2(\frac{g}{2}\sqrt{n+1}t)$$
(25)

For n=0, g is called the vacuum Rabi frequency.¹¹ The strong coupling effect can also be modeled by the coupled oscillator model that we introduced earlier.

When a QD is strongly coupled to a gap plasmon (cavity), then, energy will oscillate multiple times between the QD and a gap plasmon before the energy is lost, as illustrated in Figure 14. This variation of probability in time (Rabi oscillation) can also be Fourier transformed into the energy space, and the double-peak spectra (Rabi splitting) can be seen.



Figure 14 a Illustration of the state of the system. **b** Probability of finding the system in the excited state with no photons in the cavity with respect to time. **c** The spontaneous emission spectra of the system, which can be seen as a Fourier transform of **b**. g is the coupling strength between the cavity and the two-level system. *Permission granted, adopted from ref*²⁷, [*Khitrova, G. Nature Physics 2006, 2 (2), 81–90*]. *Copyright Springer Nature 2006.*

The illustrations in Figure 14 include the damping that will occur in a realistic system. To take this damping into account, the interaction between the emitter and the cavity can be described in a rate diagram, shown in Figure 15. The energy of the emitter can either be emitted as a photon or couple to the plasmonic cavity. The coupling can result in either a side emission (R_1) or a forward emission (R_2).



Figure 15 Schematic description of a lossy two-level emitter interacting with a single mode in a leaky optical cavity. go is the coupling constant between the emitter and the cavity field. $A_{\vec{p}}, A_{\vec{p}}^*$ and $B_{\vec{k}}, B_{\vec{k}}^*$ are the coupling constants between the emitter, a single photon, and their respective reservoir fields (R_1, R_2). ¹⁰ Reprinted with permission from [Guoqian Cui, Phys. Rev. A 73, 053807 (2006)]. Copyright (2006) by the American Physical Society.

The system in Figure 15 can be represented by a state vector consisting of the emitter state and the cavity states (R_1 and R_2). The probability amplitude of the system in each specific state can be solved. Lastly, the emission spectra are obtained by taking the Fourier transform of the probability amplitude. The derivation of this model is beyond the scope of this thesis, therefore I simply present the result for the forward-emission photoluminescence:¹⁰

$$PL(\omega) = \frac{\gamma_{\rm SP}}{\pi} \left| \frac{-i(\frac{g}{2})}{\left(\frac{\gamma_{\rm SP} + \gamma_{\rm QD}}{4} + \frac{i(\omega_{\rm QD} - \omega_{\rm SP})}{2} - i(\omega - \omega_{\rm SP})\right)^2 + {g'}^2} \right|^2$$
(26)

where
$$g' = \sqrt{(\frac{g}{2})^2 + (\omega_{\rm QD}/2 - \omega_{\rm SP}/2)^2 - (\gamma_{\rm SP}/4 - \gamma_{\rm QD}/4)^2}$$
. For the coupled plasmon-QD system, Eq (26) corresponds to photoluminescence that is coupled from the QD into the plasmon resonance, and is subsequently radiated by the plasmon into free space. From this analytical model, it is shown that two slightly different emission spectra exist in a cavity that strongly couples to an emitter.

Eq (26) was used in my study to calculate the photoluminescence spectra, by first generating the parameters from the scattering spectra fit (Eq 20). We noticed some minor differences between the measurement and Eq (26), and we believed these differences might be a result of the oversimplifications used in Eq (26). The main difference between the model and our experiment was the assumption that the radiation is coupled from the QD into the plasmon resonance, and was then radiated to free space. But there was also radiation directly from the QD into free space. In practice, the two would have different radiation patterns, and we would need to take into account the directions from which we collect the emission. This is something that could be done in principle, but it would require a rather involved simulation.

So far, we have discussed the theory of strong coupling between an optical cavity and a single emitter. However, in the case of *N* emitters coupling to an optical cavity, the coupling strength is no longer *g*, instead, the coupling strength is $\sqrt{N}g$.²⁸ Because of this \sqrt{N} scaling, more emitters in the cavity will lead to a larger coupling strength. However, as explained below, strong coupling with a single emitter enables applications, particularly in quantum information processing, that are not possible with multiple emitters.

1.2.6.1 Achieving strong coupling between a quantum dot and gap plasmons

To observe strong coupling in experiments, the time it takes to transfer the energy from the two-level system to the cavity needs to be shorter than the lifetime of both the twolevel system and the cavity, otherwise the energy will be lost before a complete transfer. The higher the decay rate, the quicker the energy will be lost in a system. Different systems have different decay rates. In this study, the two-level system will be semiconductor nanocrystals, also known as quantum dots (QDs). The lifetime (inverse of the decay rate) of a QD is on the order of a nanosecond (10^{-9} s).²⁹ In contrast to the QD, the lifetimes of gold or silver nano-cavities are on the order of tens of femtoseconds to hundreds of femtoseconds (10^{-14} s ~ 10^{-13} s).³⁰ So, the decay rate in a strongly coupled system should be on the order of 10^{13} s⁻¹. In practice, it is hard to measure an energy transfer on a tens of femtoseconds scale.³¹ To solve this problem, we measured strong coupling in the spectral space, which is the Fourier transform of this energy transfer process. In the spectral space, there is a double-peak feature in the spectra; this feature can be easily resolved by modern spectroscopic techniques.^{3,32–34}

1.3 Justification for my thesis

1.3.1 Research questions

• Can I find the "dip" or the double-peak feature in the scattering spectra of a plasmonic structure coupled with a QD, as predicted by the theoretical studies?

- Can I overcome the ambiguity in scattering measurements between intermediate and strong coupling?
- Can I control this interaction/coupling by a laser? For example, could I switch the scattering of a plasmonic structure coupled with a QD from the left of Figure 16 to the right of Figure 16, and *vice versa*.



Figure 16 Calculated scattering spectra using a classical coupled oscillator model. The first research question is that whether we can observe the predicted splitting in the measurements (right panel). The second question is that whether we can be sure that the splitting is generated from the strong coupling effect, not anything else. The last question is whether we can reversibly control the coupling (from left to right).

1.3.2 Challenges

Achieving strong coupling between QDs and plasmonic cavities (gap plasmons) is challenging. There are three major issues that need to be solved, shown below in Figure 17.



Figure 17 To achieve strong coupling, we need **a** a precise control of the relative positions, **b** a control of the number of QDs involved in the coupling, and **c** specific geometries of the gold nanoparticles, for example, forming dimers of GNPs. QD is shown in red and GNP is shown in yellow.

First, we need to precisely control the spacing between the QD and the GNP. QDs are generally less than 10 nm in diameter and gold nanoparticles are around 100 nm in diameter. As explained above, the QDs need to be very close to the gold nanoparticles to exhibit strong coupling (about 1 nm).^{4,8,35,9,36,37} As a result, we need to have a 1 nm scale control over the relative position of the particles. An illustration is shown in Figure 17a.

Second, we need to limit the number of particles involved in the process. Even though it is easier to achieve strong coupling with many emitters, a single emitter must be coupled to the plasmon in order to achieve the single-photon nonlinearities that will enable novel application.³⁸ As explained below, a single coupled emitter-plasmon system can enable single-photon gates and other applications that are not possible when multiple emitters are involved. An illustration is shown in Figure 17b.

Third, strong coupling also depends on the energy difference (detuning) between the QD band gap and the plasmonic mode. The plasmonic mode depends on the structure and geometry of the GNPs. For example, a dimer of gold nanorods tends

to have a plasmon mode at lower energy compared to the plasmon mode of a pair of GNPs. Our chemist collaborator can tailor the plasmon resonance to match the resonance of the QD by changing the shape of the GNPs. An illustration is shown in Figure 17c.

Besides the difficulties in sample preparation, performing measurements on a system consisting of a QD and a gap plasmon is not trivial. Because of the challenges in sample preparation, the yield of the sample is often low. If we measure the ensemble, signals from failed samples will bury the useful signal. As a result, we need to use a single particle microscopy method to locate the few successful particle assemblies out of hundreds of unsuccessful ones.

I worked closely with our collaborators to tackle these difficulties. We found several useful architectures to achieve strong coupling effect between a single QD and a plasmonic cavity. Additionally, I developed a correlated single particle microscopy process for this task, which was based on the process Dr. Pelton used in Argonne national lab.³⁹

1.3.3 Research results

My thesis work provided clear experimental data on the interaction/coupling between a single QD and gap plasmons. This data confirmed that strong coupling can happen between a single QD and gap plasmons. In addition, the data showed that there were three different regimes of coupling between the single QD and the gap plasmon. A calculation of these three regimes are shown in Figure 18. In the weak coupling regime, the emission rate of the QD was greatly enhanced due to the higher density of states created by the gap plasmon (Fermi Golden rule).²³ In the intermediate coupling regime, the Fano resonance was seen, which was previously predicted by others in theoretical studies.^{8,35} In Fano resonance, the splitting between the normal modes (in eV) is smaller than both the linewidth of the QD and the linewidth of the gap plasmon. The dip shown in Figure 2 is a result of Fano resonance, because the splitting is smaller than the width of the gap plasmon resonance. This Fano resonance was often confused with the strong coupling resonance in previous experimental studies. In the strong coupling regime, we saw splitting in both the scattering and photoluminescence spectra of the coupled system. Furthermore, the splitting is larger than the linewidth of both the QD and the gap plasmon, showing that that system is strongly coupled.



Figure 18 Predictions for coupled QD / gap-plasmon systems in three different coupling regimes. **a** Weak coupling, **b** intermediate coupling (Fano interference), **c** strong coupling (Rabi splitting). The predicted scattering spectra (blue) and photoluminescence spectra (green) are calculated according to analytical models using the coupling strengths shown in the insets. The scattering spectra were calculated using a classical coupled oscillator model.⁴ The photoluminescence spectra were calculated using a simplified analytical quantum mechanical model.¹⁰

I worked closely with our collaborators to test multiple new approaches to fabricate the sample with a single QD in the gap. In the end, we found two robust methods to achieve single QD strong coupling with a gap plasmon:

- In the first method, Dr. Daniel's group from UMBC first chemically linked QDs on a GNP, and then I deposited these assemblies on a smooth silver film. By chance, some assemblies ended up with a QD located in the gap between the GNP and the silver film. An illustration of this method is shown in Figure 19a. I measured the sample assembly by assembly, finding several assemblies showing features of a strong coupling effect. The results of this method will be discussed in Chapter 4.
- In the second method, I first deposited the QDs, embedded in alumina, on a gold film. Then, our collaborator from University of Colorado used a gold tip to scan over the QDs, using techniques from near-field scanning optical microscopy. An illustration of this method is shown in Figure 19b. When the gold tip is on top of a QD, the gap plasmon, which was formed by the tip and the gold film, strongly coupled to the QD. A reversible strong coupling was seen by Dr. Raschke's group. The results of this method will be discussed in Chapter 5.



Figure 19 Two successful methods to achieve single QD strong coupling with a gap plasmon are shown. **a**. The QDs were chemically linked to the GNP (100 nm), then deposited on a silver film. **b**. The QD were deposited on a gold substrate, then a gold tip scanned the substrate to form a gap plasmon. The measuring method is reffered as Tip-enhanced photoluminescence (TEPL). The gap plasmon created by the tip and the film interacts strongly with the QD (exciton). The QD was coated with a 0.5 nm thick Al_2O_3 . The excitation light comes in the direction of *k*. The separation between the QD and the gold tip was controlled by varying the thickness of the Al_2O_3 spacer. Image b from Dr. Kyoung-Duck Park, the draft is under review.

1.3.4 Applications

In the weak-coupling regime, a single QD coupled to a cavity can be used to emit single photons on demand with little dephasing.⁴⁰ These single photons might be critical to quantum key distribution protocols.⁴¹

In the intermediate-coupling regime, Dr. Pelton and his colleagues previously proposed that a continuous-wave (CW) laser beam can be used to decouple the QD from the coupled system, so that the double-peak (or "dip") feature in the extinction/photoluminescence will disappear.^{4,8} For instance, it was shown in a

calculation that as the fluence of the excitation increases, the "dip" diminishes, as shown in Figure 20.⁸ Fluence is defined as the optical power density with a unit of W/cm^2 . Then, incident photons with an energy level same as the "dip" will experience a dramatic change in the probability of being scattered. In this way, we can modulate the likelihood of a photon been scattered with another beam of photons. As photons do not interact with other photons, this method provides a nonlinear way to actively modulate light with light. Based on this idea, an all-optical modulator could be realized, which could lead to a much higher modulation bandwidth compared to traditional electronic modulators.⁴²



Figure 20 a Linear absorption spectrum of a Au-CdSe-Au hybrid nanoparticle system (illustrated in the inset). Absorption spectra, σ_{abs} , are calculated using the discrete dipole approximation (DDA) and the cavity-quantum-electrodynamics (CQED) and semiclassical (SC) models. **b** Absorption spectra calculated using the CQED (dots) and corrected SC (solid) models, for ultrafast pulsed excitation. Successive spectra, corresponding to varying fluences, are displaced vertically by 2×10^{-11} cm². *Reprinted with permission from Ref* ⁸ [Shah, R. A. Physical Review B 2013, 88 (7)]. Copyright 2013 American Physical Society.

This concept can be extended to a three-level QD with two lower-energy states: a true ground state and a metastable state. This splitting could be achieved by applying a magnetic field, so that transitions from the ground and metastable states have different dipole-moment directions. If the dipole moment of the metastable state is in a different direction than that of the plasmonic cavity, the QD in the metastable state is decoupled from the plasmon, and the transparency dip disappears. Flipping the QD between the ground state and the metastable state thus turns on and off the coupling. During this flipping, the optical response of the system is modified by a single photon. This idea can thus enable single-photon transistors; an illustration is shown in Figure 21.⁴³ In this example (Figure 21), a nanowire strongly couples to a QD, and the QD can be controlled by a single photon, which determines whether photons propagating along the wire will be transmitted or reflected.



Figure 21 In this case, a nanowire strongly couples to an emitter, as a result photons will be reflected by the system. With a proper control field, a single photon can flip the emitter into a meta-stable state /s> by inducing a spin flip, which decouples the emitter from the nanowire. As a result, photons are no longer reflected by the system. Reprinted with permission from ref⁴³, Copyright © 2007, Springer Nature.

In the strong-coupling regime, similar concepts will enable manipulation of singlephoton quantum states. Photons are important in transferring quantum information, because photons do not interact with each other.¹¹ For example, it was found that a single QD in a photonic cavity could function as a quantum logic gate that can flip the polarization of incident photons.⁴⁴ In comparison with photonic cavities, plasmonic cavities can enable the strong coupling at room temperature, which is critical for future applications.

1.4 Structure of this dissertation

The thesis work is structured as follows:

- In chapter 2, first I will give an introduction to the materials and measurement methods I used in this research.
- In chapter 3, I will review the related work in this field. This review includes theoretical and experimental studies on strong coupling between an emitter and a plasmonic cavity. The review is structured such that relatively old and simple results will be discussed first, and at the end the most recent results in the field will be introduced.
- From chapter 4 to chapter 7, I will review the main results of my research, which correspond to several of my publications.
 - In chapter 4, I will discuss my most recent result on strong coupling between single QDs and gap plasmons. This work reported three different regimes of coupling between the QD and the gap plasmon, studied with correlated measurements. The synthesis was done by Brian Szychowszi from Dr. Daniel's group.
 - In chapter 5, I will discuss a similar study but with a different method and a different sample architecture. The results showed reversible strong coupling between single QDs and gap plasmons (formed by a scanning gold tip and gold film). For example, our collaborator found a double-

peaked feature in photoluminescence spectra, which is a signature of strong coupling. We worked with Dr. Gougousi's group from UMBC to prepare the sample, and Dr. Raschke's group from University of Colorado performed the measurements.

- In chapter 6, I will show a study of linked GNPs with sub-nanometer spacing. Dr. Daniel's group established the chemistry and I developed a correlated measurement method, which was used in our strong coupling studies.
- In chapter 7, I will discuss a study of electron transfer from single QDs to individual acceptor molecules. This study presents a new way to count the number of molecules on the QD through optical measurements. The QDs were synthesized by Dr. Amin from Dr. Weiss' group from Northwestern University.
- I will discuss our results and future directions in chapter 8.

Chapter 2: Methods

2.1 Overview of the experiment design

I studied the interaction/coupling between a single QD and gap plasmons. This interaction/coupling has been theoretically studied by other groups,^{4,8} so my main focus was to design, fabricate and measure a structure in which a single QD can strongly couple to the gap plasmon. As pointed out in section 1.3.2, it is hard to realize strong coupling between a QD and a plasmonic cavity. In order to achieve single-emitter strong coupling, the following requirements have to be fulfilled:

- A QD has to be positioned precisely (nm control) in a gap between two GNPs, or in a gap between one GNP and a metal film.
- The number of QD involved in the coupling should be limited to one.
- The resonance energy (emission wavelength) of the QD should match the plasmon resonance of the gap plasmon.

Based on these requirements, our collaborators and I came up with two architectures in which the strong coupling between a QD and a plasmonic cavity was observed. Illustrations of the two architectures can be found in Figure 19.

Originally, we found that we could synthesize the structure proposed by Dr. Wu⁴ by chemically linking two gold nanorods (GNRs) to a QD, with one GNR on each side of the QD; an illustration of this method is shown in Figure 22.²¹ In contrast with the structure made by lithography in a cleanroom, the chemically synthesized sample often has a more uniform crystal structure and costs less to make. Through our collaboration with Dr. Daniel's group, chemical synthesis of a QD with two GNRs were studied. Dr.

Daniel's group was able to link a QD to a single GNR (or GNP) very consistently.²¹ However, the yield of having an assembly with only one QD in the gap of two GNRs was low (right of Figure 22).



Figure 22 Illustration of preparation of assemblies with QD centers. QDs are fully functionalized with TA-sulfo-NHS. Photo from Dr. Daniel's group.

Later, we were inspired by the work from Dr. Baumberg's goup.³⁴ In their structure, they used a GNP and a gold substrate to form a small gap in which strong local fields can be generated. Instead of using two GNPs, in this case, there was only one moving part, the GNP. This structure greatly increased the yield of the sample. However, in the previous study, the authors used molecules instead of QDs. QDs are much larger than a molecule, which makes it hard to position them in the same way as a molecule. Based on our previous study, I realized that, if our collaborators first link the QDs to the GNP using the method developed by Dr. Daniel's group, then a certain fraction of the GNPs deposited on the gold film would have a QD in the gap. This approach is our first successful architecture, and an illustration of our design can be found in Figure 23. Brian Szychowski from Dr. Daniel's group did the synthesis.

Another option is to make a layer of QDs on the metal film, then deposit the GNPs on top of the QD film. However, in this scenario, thousands of QDs in the

surroundings of the GNPs will fluorescence strongly under the excitation. The signals from the QD fluorescence will bury the signal from the GNPs.



Figure 23 Fabrication of coupled quantum-dot / gap-plasmon systems. a Illustration of the synthesis process. Quantum dots (red) are linked to gold nanoparticles (yellow) through their capping molecules. The linked assemblies are then deposited on a silver film. b Electron-microscope images of linked assemblies. Quantum dots are colored in red and indicated by arrows. The left image was obtained by scanning transmission electron microscopy, and the right image was obtained by transmission electron microscopy. The scale bars are 100 nm.

In our second sample architecture, Dr. Raschke's group at the University of Colorado Boulder used a gold tip to scan over QDs on a gold film. We found that the gold tip used in tip-Enhanced photoluminescence can replace the GNP in our first architecture. Whenever the movable gold tip was on top of a QD, the tip and the gold film formed a gap plasmon. This gap plasmon strongly coupled with the QD. Molly May and Dr. Park found evidence of strong coupling in the photoluminescence spectra of this coupled system. They also found this strong coupling to be reversible. More details can be found in section 5. In the GNP-on-film structure, the sample yield is below 10%. Therefore, I had to make measurements particle by particle to find the "successful" particles. In fact, I implemented a single particle microscopy method to measure the scattering and photoluminescence.³⁹ In Dr. Pelton's lab, I spent two years to set up a home-built microscope system to make single particle measurements. Our microscope is able to measure scattering spectra of single GNRs as small as 20 nm by 50 nm, and photoluminescence spectra of single QDs can also be measured. A photo of the single particle photoluminescence (and time-resolved photoluminescence) setup is shown in Figure 24. This will be discussed in section 2.4.



Figure 24 Setup for single particle photoluminescence and time-resolved photoluminescence measurements. A 510 nm green laser was used to excite the sample. A more detailed description of the setup can be found in section 2.4 and Appendix.

2.2 Samples

Most of our samples were synthesized in solution by our collaborators from Dr. Daniel's group from UMBC and Dr. Weiss' group from Northwestern University. Other nanoparticle samples were purchased from Sigma Aldrich.

2.2.1 Quantum dots

As we discussed earlier in section 1.2.2, the emission wavelength of QDs can be controlled by varying the size of QDs in synthesis, because of the quantum confinement effect. For example, small QDs tend to emit in the green, and large QDs tend to emit in the red, as shown in Figure 25. In my study, CdSe QDs were first synthesized, and then CdS shells were grown on the CdSe cores to passivate surface states. Surface states on bare CdSe QDs can trap excited carriers, which suppresses the photon emission from the QDs. As a result, the CdS shell significantly increases the photoluminescence quantum yield of the QDs. The CdSe/CdS core/shell QDs were then functionalized with molecules that would link with the molecules on GNPs. Brian Szychowski performed the synthesis of QDs and GNPs, as well as the linking of QDs to the GNPs. The synthesis and the linking protocol can be found in our publications.^{5,21} Lastly, the linked QD-GNP sample was deposited on a metal substrate, so the QDs can couple to the gap plasmon that was formed by a GNP and a metal film.



Figure 25 CdSe QDs synthesized by Brian Szychowski. The size of the QDs increases from the left to the right in the photo. Image from Brian Szychowski.

2.2.2 Plasmonic cavities (GNPs, GNRs and gap plasmons)

2.2.2.1 Gold nanospheres

Gold nanospheres are commercially available with different sizes. The GNP scatters at a wavelength of around 560 nm in solution (depending on the size). An example is shown in Figure 26. Most colloidal GNPs have non-spherical shapes with facets. Irregularities and facets in the GNP can induce a strong near field when coupled with a metal film. These irregularities and facets tend to make the GNP "sharper", and electrons tend to accumulate near the sharp regions, which will lead to a strong near field.



Figure 26 Measured scattering of a single gold nanoparticle (GNP) in Dark-field scattering measurement, the corresponding STEM image is shown as an insert. The GNP has an irregular shape. The particle is synthesized by Brian Szychowski.

The localized surface plasmon in GNPs can be approximated by a dipole, which is relatively insensitive to the size of the GNP. This dipole approximation has been discussed in section 1.2.3. As a result, there is not much difference in the color of the solution when the diameter of GNPs changes from 5 nm to 100 nm (20 times larger), which is shown in Figure 27.



Figure 27 Photo of GNP solutions with different particle diameters, ranging from 5 nm (left) to 100 nm (right). Only small color change is found with different GNP sizes. The photo is from nanoComposix.com.

2.2.2.2 Gold nanorods

For gold nanorods (GNRs), there is a second plasmon mode corresponding to the longitudinal oscillation of electrons along the long axis of GNRs. In this longitudinal plasmon, positive and negative charges accumulate at the two ends of the GNR. The Coulomb force between opposite charges is the restoring force that determines the resonance frequency of the plasmon, just like the stiffness of a spring. In a thinner (larger aspect ratio) GNR, the restoring force is weaker, which leads to a lower resonance frequency. An analytical model of this frequency/aspect ratio dependence can be found in a book.⁷ In applications, the GNR's longitudinal mode gives chemists the flexibility to make a sample with the desired plasmon resonance frequency, and a photo of GNRs with different aspect ratios is shown in Figure 28.



Figure 28 Solutions of GNRs with descending aspect ratios from left to right. As shown in the photo, GNRs have more variance in plasmon resonance frequency compared to GNPs. Photo from Brian Szychowski.

In our lab, I measured the scattering spectra of a single GNR and its scanning transmission electron microscope (STEM) image, as shown in Figure 29. This ability to make correlated measurements helps us to study the optical property of GNRs with minor shape changes. For example, recently, our collaborator found that the ends of the rods can be modified by chemical etching, which tunes the plasmon resonance.⁴⁵ Rods with sharp ends can be used to induce stronger electromagnetic fields, this property was studied by the correlated measurement method as shown in Figure 30.



Figure 29 Normalized scattering spectra (left) of a single gold nanorod (right). It was measured by our single particle microscope. The spectra of the halogen lamp is shown as the black dashed line. The

scattering data is shown in wavelength space (nm). The nanorod was synthesized by our collaborator Brian Szychowski.



Figure 30 a The position of the peak in the scattering spectra is linear with respect to the aspect ratio of the etched rods. The etched rods were first optically measured by single particle microscopy, then they were imaged by STEM to get the aspect ratio for individual rods. **b** A plot of the electromagnetic field enhancement (E^2/E_0^2) distribution in plasmon resonance, the intensity is in log scale. The FEM calculation was done in COMSOL. (c) STEM image of an etched rod, coated with silica. Scale bar is 50 nm.

2.2.2.3 Gap plasmon, gold nanoparticle on a mirror

I used gap plasmons in my study to couple with a QD, because gap plasmons have higher electric field concentration than that of single GNPs or GNRs. In particular, the GNP on a metal film is much easier to fabricate than an assembly of two GNPs and one QD in the middle. In my experiment, I used gap plasmons with a plasmon resonance frequency that matched the resonance of the QD; in this case, the coupling strength was maximized.

2.3 Sample preparation

In order to make the gap plasmon, I prepared a thin metal film in the cleanroom of Physics Department at UMBC. Besides a thin metal film, a dielectric thin film was also prepared, which worked as an insulator layer and a protection layer for the QD. The QDs were drop-casted on the substrate. An illustration for the sample preparation process for the tip-QD-film study is shown in Figure 31. In the GNP-QD-film study, linked QD-GNP assemblies were directly drop casted on a silver film.



Figure 31 Thin film fabrication process for gold tip strong coupling study. The details can be found in section 2.3.2. First a film of gold was deposited on a Si wafer. Second, a template stripping method was used to produce a super-smooth gold substrate. Third, a spacer layer was grown on gold by ALD. This spacer layer was used to separate the QD with the gold film. Fourth, the QDs were deposited on the spacer. Last, a capping layer was grown on QDs by ALD. The capping layer avoided direct contact between the QD and a gold tip.

2.3.1 Substrates and cleaning

In single-particle measurements, the signal from the particle of interest needs to be large compared to any background from the environment. Strong background signal can come from simply a dirty substrate. For this reason, a clean substrate is always the first step. I used glass coverslips to secure the nanoparticles for spectroscopy measurements. I discovered that the premium glass coverslips from Fisher worked the best. In fact, the glass coverslips need minimum treatment in fluorescence measurements, because most of the dust or dirt does not fluorescence as much as the QDs.

I measured the scattering of particles using a dark-field microscopy method, in which dust and dirt scatter almost as much as gold nanoparticles, or even more. The dark-field microscopy will be introduced in section 2.4.1. In this case, special care is needed to maintain a high signal to noise ratio. One of the methods is to use a piranha solution (a mixture of sulfuric acid and hydrogen peroxide) to etch the glass coverslip. This method is found to be dangerous and time consuming. After some research, I found that a strip-coating cleaner is effective in cleaning the glass slides. This process starts with coating the glass with a layer of adhesive polymer (First Contact cleaner). The coating will cure in about 30 minutes. Then, the coating is peeled off, which will remove the dust and dirt with it. An illustration is shown in Figure 32.




For the optical and SEM correlated measurement, I used silicon nitride TEM grids from Ted Pella, Inc. I found this substrate to have the minimum back scattering compared to the other electron microscope substrates (carbon ones). The thickness of the Silicon Nitride film on the TEM grids is also very important, and the 15 nm thick TEM grids performs the best.

2.3.2 Thin film fabrication

We prepared the thin metal film to form the gap plasmon with GNPs. A smooth silver film was produced by the template stripping method.³¹ First, a 100-nm silver film was deposited on a cleaned silicon wafer by thermal evaporation (2 Å/s). In the thermal evaporation process, gold or silver pellets were heated up in a tungsten boat by a high electric current. The melted gold or silver evaporated in a high vacuum and deposited on the substrate. A photo of the thermal evaporator is shown in Figure 33. Epoxy (from Ted Pella, Inc) was then applied to the silver (or gold) film and a cleaned glass slide (or a silicon substrate) was placed on the top. The epoxy was cured in an oven at 75°C

for 30 min, and then was allowed to gradually cool down to room temperature for another 30 minutes. Lastly, the glass slide (or the silicon substrate) and silicon wafer were pulled apart, leaving the silver (or gold) film on the glass slides with an ultrasmooth exposed surface, as shown in Figure 34.



Figure 33 Photo of the chamber in a thermal evaporator. Gold pellets were loaded in the boat to form a thin gold film on the substrate.



Figure 34 Photo of a template-stripped Au film (left) using epoxy. The gold film in the center on the original substrate (right) was stripped off, exposing the ultra-smooth bottom surface.

An Alumina spacer could be deposited by atomic layer deposition (ALD), which is a self-limiting process in which a single layer of atoms is deposited in each cycle. An illustration of this process is shown in Figure 35. In the first ALD process, the metal film was coated with alumina. I deposited QDs on top of the alumina layer. In the second ALD process, a capping layer was deposited on top of the QDs as well as the already coated metal film. The ALD was performed by our collaborator, Jaron Kropp.⁴⁶ For both ALD steps, trimethylaluminum (TMA) and water were used as precursors. Depositions were performed in a custom-built flow tube reactor described elsewhere.⁴⁶ The base layers were deposited at 200°C while the capping layers were deposited at 80°C to avoid thermal degradation of the QDs. Depositions occur under a steady flow of N₂. Each ALD cycle consists of, in succession: a 0.1 second TMA pulse; a 30 second N₂ purge; a 0.5 second water pulse; a 30 second N₂ purge. The growth rate of Al₂O₃ was ~1.0 Å/cycle at 200°C, and ~0.8 Å/cycle at 80°C. The number of ALD cycles was adjusted to achieve the desired dielectric film thickness. The film thickness was confirmed via spectroscopic ellipsometry (J.A. Woollam alpha-SE) measurements on companion Si wafers. In some special cases, a layer of silica was deposited on the Ag film by sputtering at a deposition rate of 2 nm/min.



Figure 35 A basic schematic of the atomic layer deposition process. In Frame A, precursor 1 (in blue) is added to the reaction chamber containing the material surface to be coated ALD. After precursor 1 has

adsorbed on the surface, any excess is removed from the reaction chamber. Precursor 2 (red) is added (Frame B) and reacts with precursor 1 to create another layer on the surface (Frame C). Precursor 2 is then cleared from the reaction chamber and this process is repeated until a desired thickness is achieved and the resulting product resembles Frame D. Image from Wikipedia by *Mcat chem446*: https://commons.wikimedia.org/wiki/File:ALD_schematics.jpg

2.3.3 Deposition of nanoparticles

Deposition of nanoparticles is one of the most critical steps in the experiment, because the sample needs to be deposited in order to result in the correct particle density on the surface. For a sample with high particle density, signals from surrounding particles will interfere with the signal from the particle of interest in a single-particle measurement. On the other hand, if the particle density is too low, it will take a long time to find particles on the substrate. At the same time, the deposition process should leave as little residues behind as possible.

There are two categories of sample that need to be deposited: QDs (mostly in organic solvent) and GNPs (in water).

- QDs are often stored in hexane solution, and the diluted hexane solution can be allowed to dry out. Another option for the solvent is chloroform, which is a more aggressive solvent than hexane, leading to better solubility of the nanoparticles, but it can leave some residues on glass coverslips. Toluene is a compromise between solubility and residues.
- GNPs in water solution tend to form large clusters when allowed to dry out. In this case, a concentrated solution of gold nanoparticles is required to leave enough particles on the substrate within a few minutes before the solution dries out. For a decent deposition of GNPs, a rule of thumb requires the concentration

of the sample to be high enough to have some color in the solution. Otherwise, the deposition time has to be very long (over 30 minutes).

More care is needed in dealing with more delicate substrates, like TEM grids. In this case, I can remove the extra solution by sliding one side of the TEM grids on the surface of deionized water. With caution, the extra solution can be quickly sucked into the deionized water, which will leave no residue behind. An illustration of this process is shown in Figure 36. In addition, the clean side of the TEM grids should not be wetted by the solution, or the solution will be trapped inside the groove and will dry out to form clusters.



Figure 36 Illustration of the sample deposition method for GNPs. The extra solution can either be blown off by air or be sucked into water.

2.4 Measurement methods

In my study, I measured the scattering spectra of single plasmonic cavities coupled with QDs. I was looking for changes in the scattering spectra of the plasmonic cavities after I put QDs in the cavities. Because of the low yield of the sample, I had to measure the scattering spectra of single particles.

I also measured the photoluminescence of strongly coupled QDs, which was different from that of bare QDs. For example, some of the photoluminescence measurements showed a double-peak feature, which is an indicator of strong coupling. Furthermore, with a pulsed laser and a single photon detector, I measured the time-resolved photoluminescence. In time-resolved measurements, the decay rates of excitons the QDs can be measured, and the change in decay rates can be used to find out whether the QDs are coupled to the plasmonic cavity. This is possible because a GNP in the vicinity of a QD can increase the decay rates of excitons in the QD.²³

In one of our studies, I correlated the scattering spectra of a particular particle with its scanning transmission electron microscope (STEM) image, which told us the relationship between the plasmon resonance and the geometry of the particles.

2.4.1 Dark-field scattering

I used a dark-field microscopy method to measure the scattering spectra of the coupled structures. In dark-field microscopy, the incident light from a lamp is modified by a series of optics to form a hollow light cone. The vertex of this hollow cone is on the substrate. Without any particles, the hollow cone of light passes through the substrate, and no light can be collected by the optical objective, thus a dark field is seen through the eyepiece or the camera. On the other hand, if a particle is present, light is scattered by the particle. The scattered light is then collected by an optical objective.

An illustration of dark-field scattering measurement is shown in Figure 37. Dark-field scattering measurement was performed on a home-built microscope, in which a dark-field objective from Nikon (TU PLAN FLUOR BD 100X) was used. First, collimated light from a halogen lamp was passed through a dark-field cube from Nikon, which blocks the center of the beam, forming a "ring" of light. Then the annular light or the "ring" was reflected into the outer column of the objective. The dark-field objective worked as a condenser to form this annular beam of light into a hollow cone. The hollow cone had a large angle with respect to the normal direction of the substrate, which is also larger than the collection angle of the objective. No (little) light is scattered back into the objective on a clean substrate. When a nanoparticle is present, light was scattered light is channeled into a spectrometer to record the scattering spectrum. The grating spectrometer (Acton SpectraPro 500i) was equipped with a CCD camera (Princeton Instruments Pixis 400). The acquisition time was set to be 5 seconds.

The dark-field scattering spectra are normalized as follows:

$$I_{normalized} = \frac{I_{raw} - I_{dark}}{I_{background} - I_{dark}}$$
(27)

where I_{raw} is the raw data for the scattering intensity, I_{dark} is the dark count of the CCD camera with no light source, and $I_{background}$ is the background scattering signal collected without the particle. The scattering intensity recorded by the spectrometer is recorded as a function of wavelength. To convert the scattering spectrum so that it is a function of energy, I have to consider the fact that the density of the points is different

for the two variables. This conversion can be done by dividing the wavelengthdependent spectrum by the square of the wavelength.



Figure 37 Setup for single particle dark-field scattering measurements.

2.4.2 Photoluminescence measurement and time-resolved measurements

I measured photoluminescence and time-resolved photoluminescence of QDs and QD-GNP assemblies. The photoluminescence spectra of emitters are measured using a fluorescence setup. In the fluorescence process, an excited electron in a sample quickly relaxes to the lowest energy state in the conduction band, then the electron returns to the ground state and emits a photon at a longer wavelength. In the experimental setup, the emitted photons from the sample can be separated from the incident or scattered laser light by using a long-pass filter, because the emitted photon is at a longer wavelength than the incident laser.

An illustration of the measurement setup is shown in Figure 38. In photoluminescence measurements, samples (nanoparticles) were excited by a diode laser (Picoquant PDL-800-D) with a wavelength of 515 nm (or 420 nm) and a pulse width of approximately 100 ps. For most measurements, the laser repetition rate was set as 40 MHz and the average power entering the objective was 0.38 mW. The laser beam was first reflected into the objective by a dichroic filter. Second, the laser beam can either be focused to a small spot, by sending collimated laser light into the back aperture of the objective, or can illuminate a large area, by using a lens in the light path to focus the laser light onto the back aperture of the objective. I can find the particles of interest in the broad-area illumination mode, then I switch to the focusing mode and bring the particle to the laser focusing spot (~5 μ m). In the focusing mode, with appropriate sample concentration, signals from only one nanoparticle are collected. Particles in the distance will not be excited because of the small laser spot. An illustration is shown in Figure 39.

Photons emitted by the nanoparticles are collected by the objective and pass through a dichroic filter (at 45 degrees) and two more long-pass filters (Semrock) to eliminate the laser beam. The filtered light is measured using the same spectrometer as for the dark-field spectral measurements.



Figure 38 Setup for single particle photoluminescence and time-resolved photoluminescence

measurements. D1 and D2 are the single photon detectors.



Figure 39 Illustration of two different optics arrangement in photoluminescence measurement. In the broad area laser mode, many particles can be seen at the same time, which is used to locate a particle. In the focusing laser mode, only one particle is measured.

Other than these measurements of photoluminescence spectra, I made timeresolved photoluminescence measurements in our lab. In a time-resolved measurement, I measured the time it took for a single QD to emit a photon after being excited by a laser pulse. During the measurement, the QD was hit by millions of laser pulses, and all the decay times between each laser pulse and each photon emission were recorded; this is known as the time-correlated single-photon counting (TCSPC) method. An illustration is shown in Figure 40.



Figure 40 An illustration of the time-resolved photoluminescence measurement. After each laser excitation, the time it takes for the sample to emit a photon is recorded. Using this recorded data, a histogram can be accumulated, which tells us on average how long it takes for the excited sample to emit a photon. Image from Photonic.com.⁴⁷

For TCSPC measurements, we used PD-050-CTD single-photon detectors from MPD and PicoQuant PicoHarp 300 timing electronics. For each detected photon, the start-stop time between the latest laser pulse and the emitted photon was recorded (in ps and ns range), as well as the real time between the emitted photon and the start of the experiment, as illustrated in Figure 41. In this mode, a large amount of data was accumulated. To save storage space on the computer, this data was saved in a binary format (ptu file). A home-made Python script could read and process the binary file. This Python script was inspired by code provided from the PicoQuant website and one of our collaborators, Victor Amin.



Figure 41 Illustration of the advanced mode used in time-resolved photoluminescence measurements. The start-stop time and real-time were recorded for each photon event. Image from PicoQuant.⁴⁸

However, the time-resolved photoluminescence data (TCSPC) needs to be processed. First, the zero-time need to be set properly. This can be done either with a physical delay circuit, or I can post-set the zero data by defining the peak of the TCSPC data as the starting point.

The photon counts can be binned into regular time intervals over the course of the measurement, giving a total count rate as a function of experimental time. These time traces show that the photoluminescence of a single QD fluctuates randomly between bright (on) and dark (off) states, which is known as "blinking".⁴⁹ When the QD is in the dark state, both radiative and non-radiative processes are responsible for exciton decay. When the QD is in the bright state, the decay is dominated by radiative recombination. I can thus set an artificial intensity threshold in the time trace (about 70% - 80% of the maximum), and select only the photons emitted when the intensity is above this threshold. The time delays of these photons relative to the corresponding laser pulse are then binned into a histogram. The resolution of this histogram was set

in the software before the experiment. For our setup, a resolution as small as 8 ps can be used, which is significantly smaller than the FWHM of the laser (~ 100 ps).

The histogram indicates the probability that the QD (when in a bright state) emits a photon at a certain time after having been excited. When only "bright-state" photons are selected, this probability distribution is well described by a single exponential function:⁵⁰ $I(t) = Ae^{-t/\tau} + I_{back}$. Taking the logarithm of I(t), the nonlinear data can be expressed as

$$\ln(I(t) - I_{back}) = -\frac{1}{\tau}t + C$$
⁽²⁸⁾

Eq (28) allows us to fit the data linearly to obtain τ , which is the inverse of the radiative recombination rate of a QD. In Python, a linear model can be fit by a least-squares fit or a curve fit from the Scipy package. For example, the QD shown in Figure 42 had a lifetime τ around 25 ns.



Figure 42 (a) Single particle photoluminescence of a CdSe/CdS QD. (b) The TCSPC data (time-resolved photoluminescence) of this specific QD, the lifetime from the fit is 26 ns.

2.4.3 Transmission scanning electron microscope

TEM images were acquired using an FEI Morgagni M268 TEM instrument with a Gatan Orius CCD camera, at an electron beam energy of 100 keV. In contrast, scanning transmission electron microscopy (STEM) images were acquired using an FEI Nova NanoSEM 450, at an electron beam energy of 30 keV. The spot size was chosen as 1 (arbitrary unit). A photo of the NanoSEM 450 at Department of Physics UMBC is shown in Figure 43.



Figure 43 Nova NanoSEM 450 from Department of Physics. Photo from Department of Physics, UMBC.

2.4.4 Correlated measurements

In correlated measurements, I connect the optical property of each single particle with its geometry (STEM image). From the correlated STEM image of the particle, we can see the size of the particle and whether there is any QD attached to the particle. An example is shown in Figure 44, where the scattering spectra of a GNP with some QDs were measured, along with its geometry in STEM.



Figure 44 Correlated measurement for a QD-GNP assembly. The GNP (~ 100 nm) and some QDs (less than 10 nm) are shown in the STEM image. The scattering spectra were measured (blue).

I took optical scattering measurements with the particles on Silicon Nitride TEM grids from Ted Pella. A 15 nm thick Silicon Nitride substrate seemed to work the best for optical measurements. Besides high quality TEM grids, a good nanoparticle density (~ 30 particles in a 100 μ m by 100 μ m window) on the TEM grids is also important for successful correlated measurements. An illustration is shown in Figure 45. In our setup, an Alio (AI-CM-5000-050-XY) XY stage is controlled by the LabVIEW program, which has an encoder that can tell the location of the particle

relative to the frame of the TEM grids. In our lab, I took optical measurement of the particles and recorded the positions of these particles with respect to the corners of the grids, then I used the pattern of the particles on the TEM grids to find the same particle in the STEM. For this reason, smaller grid windows helped to locate the particles in the STEM. This process is shown in Figure 45.



Figure 45 In each of the window of the TEM grids (left), there were around 20 particles. The relative positions of the particles were recorded, a map of particles in one window is shown in the middle. The scattering or photoluminescence were measured for each particle. Using this pattern, I can easily find the individual particles in STEM (right).

2.5 Numeric simulations

Numerical simulation can help us understand the optical properties of complex plasmonic structures. There are many numerical tools available to simulate the scattering of nanoparticles, such as the finite element method (FEM), the finitedifference time-domain (FDTD) method, the boundary element method (BEM), and the discrete dipole approximation (DDA).

Among those methods, the FEM is a good compromise between performance and complexity. The FEM is a numerical simulation method for solving partial differential equations with boundary conditions. First, the FEM calculation divides a large object into small elements, then it solves the equations for the small elements and combines them to form a solution for the large object. In the solving process, various approximate solutions are tested, until convergence has been reached. In our case, FEM can have a very high mesh resolution at the locations where the electric field varies quickly, while keeping a low resolution in the regions where the field is more uniform. The ability to use this non-uniform meshing greatly reduces the computation time, compared to methods such as FDTD that use a fixed mesh. An illustration of a FEM calculation is shown in Figure 46.

The FEM was implemented by using a commercial software called COMSOL Multiphysics (version 5.3a), in which we use the frequency domain interface to solve Maxwell's equations. The field is expressed in time-harmonic form:

$$E(x, y, z, t) = E(x, y, z)e^{j\omega t}$$

$$H(x, y, z, t) = H(x, y, z)e^{j\omega t}$$
(29)

Since the second derivative of time can then be replaced by ω^2 in the differential equations, we get

$$\nabla \times (\mu^{-1} \nabla \times \boldsymbol{E}) - \omega^2 \varepsilon_c \boldsymbol{E} = \boldsymbol{0}$$
(30)

This equation is then solved by the solver built inside of COMSOL. More information about COMSOL can be found in the user's guide. On our workstation, where the COMSOL simulation can automatically use up to 20 cores to speed up the calculation, the calculation usually takes around 20 minutes to an hour, depending the domain size and resolution.

The scattering of nanoparticles in COMSOL can be set up in simple steps. First, we need to choose the wave-optics module, or RF module. We also need to choose the frequency domain, which can help us understand the wavelength dependency of the plasmon resonance. Second, we can define the geometry of the particles. For each geometric object we create, the corresponding frequency-dependent refractive index (n for the real part, and k for the imaginary part) can be defined by either using the Drude-Lorentz model or by directly loading parameters from the built-in database. Tabulated dielectric function of bulk gold or silver can be easily found.^{51,52} Third, we need to define a proper mesh. The mesh needs to be fine enough to generate reasonable results. Fourth, we calculate the scattered field. Fifth, we set up the surface integral of the Poynting vector of the scattered field. This integral gives us the scattering spectrum of the nanoparticle. Finally, we can run the simulation by sweeping the wavelength to get the spectra. A more detailed procedure can be found in the Appendix.



Figure 46 Distribution of the scattered field of a gold nanorod, calculated in COMSOL.

Coupled emitter / metal-nanoparticle samples can also be simulated by the FEM method using COMSOL. However, it is difficult to properly define the dielectric function of the emitter. For CdSe QDs, the bulk dielectric function is not appropriate for a QD with a size of less than 10 nm. The optical property of a small CdSe QD is quite different from the bulk CdSe due to the quantum confinement. In this case, an empirical Lorentzian model was proposed by Wu in the FDTD study, and was adopted in our FEM simulation as well:⁴

$$\varepsilon_{QD}(\omega) = \varepsilon_{\infty CdSe} - f \frac{\omega_{QD}^2}{\omega^2 - \omega_{QD}^2 + i\gamma_{QD}\omega}$$
(31)

where $\varepsilon_{\infty CdSe}$ is the bulk CdSe dielectric constant, f is the oscillator strength, ω_{QD} is the resonance frequency of the specific sized QD, and γ_{QD} is the linewidth of the QD. In this model, most of the parameters are constrained by independent experimental measurements, except for the oscillator strength f, for which some uncertainty remains.

Chapter 3: Literature review

3.1 Introduction

The research on strong coupling between emitters and plasmonic cavities has attracted much interest recently. Several well-written review articles have been published in this field, with slightly different focuses.^{27,28,53–55} In general, there are three main parameters to be considered:

- Types of emitters
- Types of cavities
- Types of measurement methods

These three aspects of strong coupling will be discussed in the following sections. Through this literature review, I will discuss how other studies handled these three aspects. This review is structured such that relatively simple systems will be discussed first, and the most complex systems are introduced at the end. These complex studies focused on strong coupling between a single QD and a plasmonic cavity. I believe my thesis work contributed to our understanding of the strong coupling between a single QD and a plasmonic cavity.

3.1.1 Emitters in strong coupling

The coupling strength between an emitter and an optical cavity (including a plasmonic cavity) can be determined by the dipole approximation:

$$g = \boldsymbol{\mu} \cdot \boldsymbol{E} \tag{32}$$

where μ is the dipole moment of the emitter and E is a "vacuum" field whose strength is equivalent to one photon in the cavity mode. The dipole moment is a property of the emitter, and the local electric field will be determined by the cavity and the positioning of the emitter inside the cavity. To achieve strong coupling (a large g), we need to have an emitter with a large dipole moment and place the emitter in a cavity that strongly localizes the electric fields. QDs tends to have large dipole moments, and cavities that are formed by plasmonic structures confine light to nanometer-scale volumes, leading to large "vacuum" fields E.

Early on, the emitters used in strong coupling studies were Rydberg atoms and micro-cavities were used.^{56,57} With time, more researchers started to use more complex emitters coupled to optical micro-cavities, including J-aggregates,^{58–60,31,61–69}, two-dimensional materials,^{70–72} and QDs.^{73–77,32,78,3,33}

A good candidate for an emitter in a strong-coupling study needs to have the following properties:

- It should have a large dipole moment.
- It should be easily incorporated into a cavity.

A list of common emitters with their corresponding dipole moments can be seen in Table 1. Atoms are small, and they fill optical cavities easily.⁷⁹ However, it is hard to achieve single-atom strong coupling, because of the small dipole moment of the atoms.

J-aggregates are formed by dye molecules, and have a narrow absorption band that is red-shifted compared to the absorption band of the monomers that make up the aggregates. J-aggregates are relatively easy to incorporate in to cavities as well, and they have a relatively large dipole moment. ^{58–60,31,61–69} The use of J-aggregates enabled many studies with different plasmonic structures.

2D materials are straightforward to incorporate with surface-plasmon cavities, as they can be deposited directly on top of a gold film. However, it is almost impossible to achieve single-exciton strong coupling in 2D materials, because of the large size of 2D materials (many excitons involved). An exciton is a bound state of an electron and a hole, which can be generated by absorption of a photon.

A QD has one of the largest dipole moments; however, it is more difficult to incorporate QDs into cavities than other emitters. Many ingenious methods have been developed to achieve single-QD strong coupling with plasmonic cavities. I will review these methods in the following sections.

Type of emitters	dipole moments (Debye)
Atoms ⁵⁵	~1
Isolated methylene blue molecules ³⁴	3.8
J-aggregates ⁸⁰	~10
2D materials (WS ₂) 81	~10
QDs ⁸²	20~100

 Table 1 List of common emitters with various dipole moments

3.1.2 Cavities in strong coupling

Early strong-coupling measurements were based on micro-cavities. The local electric field in the cavity can be written $as^{28,55}$

$$E \sim \sqrt{\frac{1}{V_m}} \tag{33}$$

where V_m is the cavity mode volume. A small mode volume helps to confine the electric field and promote strong coupling, and a table of common mode volume of different cavities is shown in Table 2. In the traditional micro-cavity study, the relatively large mode volume limited the strong coupling; the splitting is so small that it has to be measured at a low temperature, because at low temperature the QD has lower loss rate. ^{27,83} In order to achieve a higher coupling strength, the mode volume of the cavity needs to be as small as possible. Plasmonic cavities can offer a mode volume much smaller than the cube of the wavelength of light.^{7,55,84} As a result, plasmonic cavities allow strong coupling at room temperature. In addition, unlike the micro-cavities, where the bandwidth is so narrow, plasmonic cavities have a broad bandwidth, which can be helpful in applications. I therefore chose a plasmonic cavity in my thesis to couple with single QDs.

nanocavity	$V_m, \mu m^3$
photonic crystal cavity ⁷³	0.04
microdisk cavity ⁷⁵	0.07
single gold nanoparticle ²⁸	10-5
gap plasmonic cavity ³⁴	10-6

Table 2 Common mode volume of various cavities.

3.1.3 Measurements in strong coupling

Most researchers studied the strong coupling effect by measuring:

- Reflectivity (or transmission)
- Dark-field scattering
- photoluminescence

Because the surface plasmon is formed on the surface of a metal film, researchers often measure the reflectivity in surface-plasmon studies.^{85–88,31}

In measurements on ensembles of metal nanoparticles, the extinction spectra of the sample solution are often measured.^{58–60,62,89,90} For single-nanoparticle measurements, dark-field scattering is the common measurement method.^{60,63–66,69,71,72,91–93}

As pointed by some authors, a photoluminescence measurement should be the most definitive method to probe the strong-coupling effect in plasmonic cavities.²⁷ Unlike dark-field scattering, which is sensitive to the structure of the plasmonic cavity, photoluminescence measurements are immune to irregularities in the plasmonic caivity.^{33,67,69,70,73–75,78,89} As we discussed earlier, Fano interference is a coherent process; if the coupling strength is in the intermediate regime, the Fano dip will be observed, but not the splitting in photoluminescence because photoluminescence is an incoherent process.

Besides reflectivity, scattering and photoluminescence measurements, recently, a study found Fano resonance between emitters and a plasmonic cavity by using a scanning tunneling microscope (STM).⁹⁴

3.2 Excitons coupled to surface plasmons

The sample preparation involving surface plasmons is the most straightforward in the field, because surface plasmons are generated by electron oscillation at the interface between the metal film and dielectric materials, and emitters (such as J-aggregates) can be coated on the metal surface.^{31,36,85,87,88,95} The metal film, either gold or silver, can be deposited on a glass prism. This enables measurement of the reflectivity with different incidence angles of excitation. The incidence angle of the excitation light tunes the surface plasmon resonance by tuning the wave vector of the incident photons, and thus of the plasmons that are excited. Tuning the surface-plasmon frequency modifies the detuning in the coupling; an example is shown in Figure 47. In this example, as the surface plasmon resonance energy (green) was tuned from 1.9 eV to 2.2 eV, a splitting in the reflectivity was observed (orange), which is a sign of strong coupling between the surface plasmon and CdSe film.



Figure 47 (A) Reflectivity spectra measured for a Ag/CdSe film with nanocrystals of ~4.3 nm in diameter. The angles of incidence are indicated in the figure. For this CdSe film, the parameters obtained for the Lorentz model are: $\hbar\Gamma = 0.187 \text{ eV}$, $\varepsilon_b^{1/2} = 1.89$ and f = 0.07. (B) Normal incidence absorption spectrum of a film of the CdSe nanocrystals. The vertical line indicates the $1S_{3/2}(h)1S_e$ exciton transition. (C) Experimental dispersion curve (dots). The energy position of the reflectivity minima is on the vertical axis and the external angle of incidence on the horizontal one. The green line is the energy of the uncoupled SP, the red line corresponds to the position of the $1S_{3/2}(h)1S_e$ exciton transition, and the orange lines are obtained from a fit with $\hbar\Omega_R \sim 102 \text{ meV}$. *Reprinted with permission from* ⁹⁶. [Gómez, D. E. Nano Letters 2010, 10 (1), 274–278].Copyright 2010 American Chemical Society.

3.3 Excitons coupled to ensembles of nanoparticles

Unlike the coupling between emitters and surface plasmons, only a limited number of emitters will couple to metal nanoparticles, because of the small size of metal nanoparticles. In this case, a more delicate sample preparation method will be needed.

It was discovered that molecules (emitters) can be chemically attached on the surface of gold nanoparticles.^{59,67,70,78,90,91,93} This process was a step forward towards

single-particle strong coupling. The measurements are often done in solution, because of the relatively high yield. An example is shown in Figure 48, where a layer of Jaggregates was coated around the GNR, and a splitting in the photoluminescence (red) and the extinction (blue) of the sample solution was observed.



Figure 48 An illustration of excitons coupled to ensembles of nanoparticles. *Reprinted with permission*⁶⁷. [Melnikau, D J. Phys. Chem. Lett. 2016, 7 (2), 354–362] Copyright 2016 American Chemical Society.

3.4 Excitons coupled to single nanoparticles

Because of the difficulties in sample preparation, the yield of the sample is often low. We can study the coupling using single particle dark-field microscopy,⁷ which allows us to study the strong coupling effect at a single particle level regardless of the yield. Various types of plasmonic particles have been studied by other groups using single particle dark-field microscopy, including gold nanorods,^{63,71} gold nanodisks,⁶⁴ silver nanorods,⁷² silver nanoparticle dimers,⁹⁷ silver triangles,^{65,69} and Au/Ag cuboids.⁹² An example of splitting in the scattering of a single silver triangle coated with J-aggregates is shown in Figure 49.



Figure 49 Dark-field scattering spectra of an uncoupled plasmonic Ag nanoprism (cyan) and a coupled single nanoprism plexciton structure (blue). Insets display SEM images of the nanoparticles imaged on top of Au surface to visualize J-aggregate shell (right) as well as graphical sketches of the nanoprisms with J-aggregates shown in red. The splitting reaches nearly 400 meV, a value significantly above the full-width at half-maximum of an uncoupled nanoprism. *Reprinted with permission* ⁶⁹. [Lee, B. Nano Letters 2015, 15 (5), 3646–3653].Copyright 2015 American Chemical Society.

Interestingly, in one study⁹², Au/Ag cuboids were coated with a layer of Jaggregates. Because of the large confinement of the field (small mode volume), the authors claimed only few J-aggregates couple to the plasmon mode of each nanoparticle. A calculation in the paper supported this claim.

Another impressive set of studies focused on the strong coupling between transition metal dichalcogenide (TMD) materials.^{98,99} A few monolayers of the TMD material can be generated by exfoliation⁷² or chemical vapor deposition (CVD).^{70,71} In

these studies, the scattering spectra of the plasmonic nanoparticles were found to have the two-peak feature. However, as pointed by Baumberg group²² in their study of strong coupling between TMD materials and the plasmonic cavities, there are three difficulties in this field: (a) the coherence size of the exciton in TMD materials is much larger than the mode volume of the plasmonic cavities; (b) most of the dipole moments of monolayer TMD materials are parallel to the film, which is hard to couple to the vertically-polarized gap plasmon; and (c) it is hard to obtain a large enough coupling strength without tuning the plasmonic resonance into the infrared.

In our study, we found another difficulty related to measurements with TMD materials. We found that some common TMD materials have two peaks in their reflectance spectra around 2 eV, as shown in Figure 50.¹⁰⁰ This two-peak feature is attributed to a splitting by spin-orbit coupling. As a result, the scattering spectra of the plasmonic nanoparticles can be contaminated with the two-peak reflectance signal of the TMD materials. It will thus be difficult to determine whether the two-peak feature is a result of strong coupling or just the reflectance of the TMD film. The four most commonly used TMD materials, MoSe₂, WSe₂, MoS₂ and WS₂, all suffer from this problem.



Figure 50 (a) Comparison of the reflectance spectra of two different exfoliated MoS₂ monolayers. (b) Comparison of the reflectance spectra of exfoliated (red) and CVD-grown (blue) MoS₂ monolayers. *Reprinted figure with permission from ref*¹⁰⁰, [Li, Y. Physical Review B 2014, 90 (20)]. Copyright 2014 by the American Physical Society.

3.5 Single excitons coupled to single nanoparticles

As discussed in section 1.2.6, it is easier to achieve strong coupling with many emitters, because of the \sqrt{N} scaling of the coupling strength. However, single-emitter strong coupling enables many special applications, including single-photon quantum gates and on-demand single-photon sources.^{38,40} On the other hand, it is particularly challenging to achieve strong coupling in a plasmonic cavity system with only one emitter. In order to achieve this, we need to place emitters close to the plasmonic structure to have a substantial coupling strength, while keeping only one emitter coupled. In some sense, it is a nano-engineering problem. I will review the most recent progress in this field. There were some exciting results reported in the last few years; however, there is still a long way to go to have real-world applications.

3.5.1 Coupling between one QD and one GNP, enabled by AFM positioning³²

In one study,³² the author used an AFM tip to move GNPs around. The researcher moved the GNP to a place close to a QD. The change in the QD decay curve after the GNP movement showed that the GNP is indeed very close to the QD, because a GNP in the vicinity can speed up the decay rate of a QD.²³ Instead of seeing the strong coupling effect, the author reported a Fano resonance line-shape. In this Fano resonance line-shape, a relatively small change in the GNP scattering was seen. This result is shown in Figure 51, where the scattering of a GNP was modified by the presence of a QD (from left to right).



Figure 51 Scattering and anisotropy of a plasmonic cavity (i.e., an MNP) controlled by a single QD. (A) Experimental schematics for scattering measurements. (B) Experimentally measured absorption (black)

and photoluminescence emission (red) spectra from an ensemble of colloidal CdSe/ZnS core–shell QDs. (C) Measured scattering spectra of a bare 30-nm-diameter MNP at different analyzer angles. The small changes near 550 nm or below are likely due to deviations from a perfectly spherical shape of the MNP. (D) Measured scattering spectra of the assembled QD–MNP hybrid structure at different analyzer angles. The Fano resonance indicated by the dotted vertical line spectrally aligns with the lowest exciton state measured in the absorption from an ensemble of QDs. The Fano resonance is most pronounced at $\phi_A=30^\circ$. Reprint permitted, copyright (2015) National Academy of Sciences.³²

The result is exciting, yet not complete. First, it is surprising that the author did not use a QD that would match the plasmon resonance of the GNP. Usually, a zero detuning between the QD resonance mode and GNP plasmon resonance mode will generate stronger coupling. Second, after the AFM manipulation, there is no guarantee that the orientation of the GNP was maintained. The GNP could have perfect symmetry in one plane, as shown Figure 51 C, but if it was rotated, it might not be symmetric in another plane, which could generate the spectra in Figure 51 D.

3.5.2 Single molecule strong coupling with gap plasmons³⁴

In work from Dr. Baumberg's group, the authors used a robust gap-plasmon structure to achieve strong coupling at the single-molecule level,.^{34,101} Specifically, molecules were placed in the gap between a GNP and a gold film, as shown in Figure 52.



Figure 52 a Scattering spectra resulting from isolated NPoMs according to the orientation of the emitter (the methylene-blue dye; see insets). With the dye transition dipole moment, μ m, oriented parallel to the mirror, the resonant scattering plasmonic peak (ω_p) is identical to that of NPoMs without any emitters. With μ_m oriented parallel to the mirror, split peaks result from the strong interaction between the emitter and the plasmon. The blue dashed line indicates the dye's absorption wavelength (centred at ω_0). **b**, Comparison of scattering spectra from different NPoMs (see insets), whose gaps are filled by a cucurbit uril monolayer that is empty (top), or encapsulating dye molecules (bottom). **c**, Resonant positions of methylene-blue (ω_0), plasmon (ω_p) and hybrid modes (ω_+ and ω_-) as a function of extracted detuning. The symbol size depicts the amplitude in scattering spectra. Reprinted from ref³⁴ with permission, copyright (2018) Springer Nature.

The result showed that, by gradually decreasing the density of the molecules (emitters), single-molecule strong coupling can be achieved.⁵³ However, the splitting for the single-molecule case was only around 90 meV, which was smaller than the FWHM of the plasmon resonance. For better strong coupling results, larger oscillator strength is required, such as the oscillator strengths provided by QDs.

3.5.3 Single QD strong coupling with gap plasmon³

Single QD strong coupling is hard, because of the difficulty in positioning the QD inside the plasmonic cavity. In one study, the authors used a bowtie plasmonic structure made by a cleanroom lithography technique. Non-through holes were made by e-beam lithography at the center of the bowtie structures. Then, the QDs were incorporated into the blind holes by pulling the bowtie structure out of a QD solution in water. The capillary force was responsible for the positioning of the QDs. The gap inside the bowtie was around 19 nm wide. A two-peak feature in the scattering spectra was seen, as a sign of strong coupling.


Figure 53 (a) Scattering spectra of bowties with (from top to bottom) one, two and three QDs in the gap, respectively. All spectra show a transparency dip due to Rabi splitting. The black lines are experimental data and the colored lines are fits to the coupled oscillator model. Inserts show the scanning electron microscope images of the bowties. The positions of the QDs are marked by red arrows. Scale bars, 20 nm (yellow). (b,c) Coupling rates as a function of gap size for bowties with one QD ((b) red symbols) and two QDs ((c) green symbols). The errors in the coupling rate values, obtained from the fitted functions, are estimated to be 2–5 meV. The continuous lines represent the numerically calculated coupling rates at two configurations along the center line of the bowtie: with the QDs almost touching one of the prisms (continuous lines) or with the QDs at the center of the bowtie (dashed-dotted lines). In the experiments, the QDs may be positioned away from the center line so that their coupling rates are lower than the

calculated lines. (d) Polarization series of the middle bowtie structure in a. As the polarization of the excitation light is rotated from the direction parallel to the bowtie long axis to perpendicular to it, the transparency dip in the spectrum gradually vanishes, indicating that it indeed originates in the coupling of the QD exciton with the longitudinal plasmon resonance of the bowtie. Reprinted from ref³ with permission.

This study is the first report that focused on single-QD strong coupling with a plasmonic cavity. The sample preparation technique was unique and effective. However, because of the small size of the bowtie structure, the quality of the structure was limited by the lithography technique. The gold particles were not perfect triangles, and they were not symmetric, as shown in Figure 53. This irregularity in the shape of the GNPs and a broken symmetry in the bowtie could produce a two-peak feature in the scattering spectra without any involvement of the QD. As we will show later, correlated photoluminescence with scattering is the best way to show a strong-coupling effect in these systems.²⁷

3.5.4 Single QD strong coupling in photoluminescence³³

In a recent report,³³ photoluminescence of strongly coupled QDs was studied. This study applied a technique similar to what our collaborator at University of Colorado did in the tip-enhanced photoluminescence measurements. A gold nano-tip was used to scan over QDs embedded in a PMMA film. A four-peak feature was seen in the photoluminescence of a single QD, which was explained as a result of charged and

neutral states of QDs, as shown in Figure 54. It is worth pointing out that there is no independent evidence for the model that is used to explain the four-peak feature.



Figure 54 (A) Illustration of the PNR probe interacting with QDs embedded in a polymer film. Left panel: The spectrum of a QD changes significantly when coupled to the slit-like PNR at the tip apex. Inset: SEM image of a nanoresonator at the apex of a probe tip. Scale bar, 100 nm. a.u., arbitrary unit. (B) Map of the electric field distribution of the resonator mode used in the experiment. The slightly different lengths of the two tines account for fabrication imperfections. The + and – signs indicate the instantaneous charge distribution highlighting the mode's weakly radiative quadrupolar character. Scale bar, 50 nm. Reprinted from ref ³³ with permission, copyright (2018) AAAS.

The result presented in this report is exciting. However, the four-peak structure that was found was unexpected. The special CdSeTe/ZnS QDs that were used had a much broader spectral linewidth in photoluminescence compared to commonly used CdSe QDs, and it is possible that the unusual four-peak feature had something to do with this particular type of QD.

In these types of measurements, a critical question is how to prove that a single QD is involved in the coupling. To address this issue, the author argued cited the small

mode volume of the gold tip and blinking in photoluminescence as the evidence. The argument of small volume is commonly used in the literature as a result of lack of more direct measurements.⁹² Indeed, it is hard to prove that only one QD is involved in strong-coupling measurements, except when using correlated optical/SEM single particle microscopy.³

Chapter 4: Strong coupling between gap plasmon (gold nanoparticles) and single quantum dots

In the last few years, I set up the necessary equipment in the lab and constantly improved the sensitivity of measurement methods. In the meantime, I explored several different routes to fabricate the samples, including making an array of 10 nm deep 100 nm wide holes on a thin gold substrate to hold QDs. However, none of the methods seemed to work, because of the low sample yield. In 2017, Dr. Daniel's group in the UMBC Chemistry department developed a method to link QDs and GNPs with GNRs. We realized that if we first linked the QDs on a GNP, and then deposited the linked assembly on a silver film, in some cases a QD could be found in between the silver film and the GNP. This gap plasmon design was inspired by work from Dr. Baumberg's group.³⁴ Because of the localized near-field distribution in the gap plasmon (GNP on a silver film), only the QD located in the small gap would strongly couple to the plasmon resonance. Indeed, I found evidence of strong coupling in the sample synthesized by Brian Szychowski. I prepared the sample on a silver substrate, then I took correlated scattering/photoluminescence measurements on single particles. Later I fitted the scattering data using a classical model (Eq 20), and the results of the scattering fit were used to generate the photoluminescence spectra using an analytical quantum model (Eq 26).

4.1 Sample preparation

The coupled plasmon-QD systems are produced experimentally as illustrated in Figure 55a. Colloidally synthesized GNPs and CdSe/CdS QDs are linked covalently through

their capping molecules, resulting in a small number of QDs on the surface of each GNP. Electron-microscope imaging shows that approximately half of the GNPs have a single QD bound to their surface, and approximately 5% are bound to more than one QD. (See Figure 55b). The linked particles are deposited on an Ag film by drop-casting; in some cases, a thin silica layer is first deposited on the Ag film.



Figure 55 Fabrication of coupled quantum-dot / gap-plasmon systems. a Illustration of the synthesis process. Quantum dots (red) are linked to gold nanoparticles (yellow) through their capping molecules. The linked assembles are then deposited on a silver film. **b** Electron-microscope images of linked assemblies. Quantum dots are colored in red and indicated by arrows. The left image was obtained by scanning transmission electron microscopy, and the right image was obtained by transmission electron microscopy. The scale bars are 100 nm.

Although strong coupling has previously been reported in a similar system,³⁴ a finiteelement numerical simulation predicts only weak coupling, see Figure 56 a and b. The simulation suggests the splitting is small compared to the overall linewidth of the plasmon resonance. Fitting the calculated spectrum (Figure 56b) to a coupledoscillator model (Eq 20) gives a coupling strength g of only 10 meV, significantly less than the 100 meV plasmon linewidth. Previous reports of others also had difficulty using realistic calculations to explain observations of single-emitter strong coupling.^{3,34} However, real nanostructures are more complex than the simple geometries used in the calculations. In particular, quasi-spherical metal nanoparticles are always faceted, and these facets can further localize fields, thereby increasing coupling strengths. Finiteelement simulations predict significantly stronger coupling for a quantum dot located between the silver film and edge of a facet or the apex of a facet on the gold nanoparticle. The facets I used in the FEM simulation were created by truncating a gold sphere with several planes, which help to generate stronger electric fields in the gap. This stronger coupling enables the system to enter the intermediate-coupling and strong-coupling regimes. (See Figure 56) The simulations also show that faceting of the nanoparticle leads to strong localization of the fields within the gap in the lateral dimensions, with the electromagnetic energy extending laterally over approximately 10 nm. Since this is less than twice the diameter of the QDs used, at most one QD can be located within the high-field region and couple to the plasmon resonance.



Figure 56 a Quantum dot located next to the gap between a spherical gold nanoparticle and a silver film.b Quantum dot in the gap between a spherical gold nanoparticle and a silver film. c Quantum dot in the

gap between the edge of a faceted gold nanoparticle and a silver film. The facets are formed by truncating a spherical particle with two planes with an angle of 55 degrees. **d** Quantum dot in the gap between the apex of a faceted gold nanoparticle (approximated as a polygon) and a silver film. The top panels show the simulated structures; gold nanoparticles are in yellow, quantum dots are in red, and silver films are in grey. The bottom panels show the simulated scattering spectra.

4.2 Weak coupling

A single-particle optical microscope is used to measure the scattering and photoluminescence, including time-resolved photoluminescence, from individual nanostructures. In the majority (approximately 98%) of the cases where photoluminescence is observed, both the scattering and PL spectra are single peaks, as illustrated in Figure 57a. The scattering spectra are comparable to those of AuNPs on an Ag film without any QDs, as shown in Figure 58, indicating that the system is in the weak-coupling regime. The PL spectra of weakly coupled QDs are comparable to those of isolated QDs (see Figure 58), apart from an additional broad background feature, which can be attributed to PL from the metal nanostructure (Figure 59).^{102,103} The narrow linewidth of the peak in the PL spectrum indicates that the photoluminescence arises from a single QD: variations in the size and shape between two or more QDs would lead to inhomogeneous broadening of the spectrum.



Figure 57 Quantum-dot / gap-plasmon systems in the weak-coupling regime. a Measured scattering spectrum (blue) and photoluminescence spectrum (green). **b** Theoretical scattering and photoluminescence spectra. **c** Time-resolved photoluminescence from the coupled system (green), obtained by time-correlated single-photon counting. The red curve shows a reference trace obtained from isolated quantum dots.



Figure 58 Reference spectra for uncoupled particles. a, Photoluminescence from several isolated quantum dots. **b**, Scattering spectra of several isolated quasi-spherical gold nanoparticles. **c**, Scattering spectra of several individual gold nanoparticles on a silver film (without quantum dots).



spectra from gold nanoparticles on a silver film, without QDs. a and b show representative examples for two different nanoparticles.

Fitting the scattering spectrum to a coupled-oscillator model (Eq 20) gives g = 10 meV, consistent with simulations (see Figure 57b). The full set of parameters obtained from the fit are given in Table 3; using these same parameters to predict the photoluminescence spectrum according to Eq (26) gives a single peak, as shown in Figure 57b. Although the plasmon-QD coupling leaves the scattering and photoluminescence spectra nearly unchanged, it increases the recombination rate in the QD by a factor of 20,²³ as shown in Figure 57c.

Table 3 : **Parameters obtained from fitting of experimental scattering spectra.** Quantum dot resonance frequency, ω_{QD} , quantum dot decay rate, γ_{QD} , plasmon resonance frequency, ω_{SP} , plasmon decay rate, γ_{SP} , and coupling strength, g. All values are in units of eV.

$\omega_{SP} = \omega_{QD} = \gamma_S$	SP YQD g
--	----------

Weak coupling: Figure 57	1.86	1.87	0.10	0.07	0.01
Intermediate coupling: Figure 60a,c	1.93	1.93	0.2	0.06	0.10
Intermediate coupling: Figure 60b,d	2.00	2.03	0.23	0.08	0.11
Strong coupling: Figure 64a,c	1.86	1.88	0.15	0.10	0.23
Strong coupling: Figure 64b,d	1.90	1.91	0.19	0.13	0.16

4.3 Intermediate coupling

A small fraction (approximately 1%) of the structures show a clear dip, or induced transparency, in the scattering spectrum; a representative example is shown in Figure 60a. Fitting the scattering spectrum now gives g = 100 meV (see Figure 60c), corresponding to the intermediate-coupling regime. Using the parameters from the fit to the scattering spectrum leads to a prediction of a single peak in the PL spectrum, located at the minimum of the transparency dip, as expected for near-resonant Fano interference.⁴ (See Figure 60c.) A similar PL spectrum is observed experimentally, with the primary differences being irregularities in the PL background from the metal nanostructure and a high-frequency shoulder that can be attributed to emission from charged-exciton or multiexciton states in the QD.^{104,105} We note that the PL linewidth is consistent with the QD linewidth used in fitting the scattering spectrum, and is again consistent with the PL arising from a single QD rather than multiple, inhomogeneously broadened QDs.



Figure 60 Quantum-dot / gap-plasmon systems in the intermediate-coupling regime. a,b Measured scattering spectra (blue) and photoluminescence spectra (green) before (a) and after (b) intense laser illumination. **c,d** Theoretical scattering (Eq 20) and photoluminescence spectra (Eq 26).

The interpretation of the high-frequency shoulder in the PL spectrum as being due to charged-exciton or multi-exciton states is supported by measurements of the power dependence of luminescence from isolated CdSe/CdS QDs. As the laser power was increased, the main peak of the QD red-shifted, and a blue peak/shoulder started to appear, as shown in Figure 61. Similar features have previously been attributed to charged and uncharged states of the QD.^{104,105}



Figure 61 Multi-exciton emission of a CdSe/CdS QD with increasing laser power. The main peak redshifts and a shoulder appears on the blue side. All spectra have been normalized for comparison.

For linked QD/ GNP assemblies, this multi-exciton emission is frequently observed, even at low laser power, as shown in Figure 62. This feature could be mistaken as the signature of the strong coupling effect. However, a stronger splitting in PL is expected in the case of strong coupling, and the expected lineshape is significantly different from this multi-exciton emission. As shown below, these predictions are confirmed in measurements of structures that exhibit strong coupling.



Figure 62 Multi-exciton emission of CdSe/CdS QDs on a GNP. The decay curve of the photoluminescence indicates that the QD is on a GNP.

This simultaneous measurement of scattering and PL spectra allows for Fano interference to be distinguished from geometric properties of the metal nanostructure that could give rise to a double-peak scattering spectrum. It also clearly shows that observing two peaks in the scattering spectrum is not sufficient to demonstrate that a plasmon-emitter system is in the strong-coupling regime.

The interpretation of the observed spectrum as due to single-QD Fano interference is further verified by modifying the QD and plasmon resonance energies. To accomplish this, the system is exposed to intense laser illumination for a fixed amount of time, and scattering and PL measurements are then made under the same low-intensity conditions as the previous measurements. The intense illumination produces an irreversible shift in the PL peak from the QD due to photo-oxidation of the QD surface,^{106,107} and the plasmon resonance of the metal nanostructure shifts due to small changes in the local structure near the gap.¹⁰⁸ (See Figure 63) After these spectral shifts, the scattering spectrum of the coupled system still shows a Fano dip with a minimum that coincides with the maximum of the PL. (See Figure 60b,d.) Since the shift in QD luminescence is due to a photochemical change, different QDs would be expected to undergo different, random shifts in their transition energies. Our observation that the PL spectrum simply shifts, without any spectral broadening, clearly indicates not only that the Fano interference arises from the QD transition, but also that it is due to coupling between the plasmon resonance and a single QD.



Figure 63 Shift of the gap plasmon under intense laser illumination. Scattering spectrum from a gold nanoparticle on a silver film, without quantum dots, before (solid line) and after (dashed line) illumination for 30 seconds with 0.4 mW of 515-nm laser light focused to a 5 μ m spot.

4.4 Strong coupling

Finally, a small fraction (approximately 1%) of the measured samples show splitting in both the scattering and PL spectra, providing a definitive demonstration of Rabi splitting.⁶⁹ Figure 64a shows a representative example; we again compare the measured scattering spectrum to a fit, and the measured PL spectrum to a prediction using the parameters from the fit. The fit gives g = 230 meV, most likely corresponding to a QD located at the apex of a faceted GNP. This local structure is critical to minimizing mode volume and achieving strong coupling.

An indication of the importance of the local structure is obtained by performing measurements on a sample with a 5-nm silica spacer layer between the Ag film and the nanoparticles. As shown in Figure 64b,d, it is still possible to obtain strong coupling in this case. This shows that the separation between the metal nanoparticle and the metal film is not a decisive factor in obtaining the field localization required for strong coupling.

In both cases, the observed splitting in the PL spectrum is larger than the splitting in the predicted spectrum. This may be due to the simplicity of the model used to predict the PL spectrum. In particular, the modeled PL spectrum corresponds to energy that is coupled from the emitter into the plasmon and subsequently radiated from the plasmon into free space; the measured spectra may also include contributions from light that is directly radiated from the emitter into free space.



Figure 64 Quantum-dot / gap-plasmon systems in the strong-coupling regime. a,b Measured scattering spectra (blue) and photoluminescence spectra (green) for two different particles directly on a silver film (a) and with a 5-nm silica spacer between the particles and the silver film. **c,d** Theoretical scattering and photoluminescence spectra.

4.5 Conclusion

In summary, the sensitivity to a local structure explains why there is a large variation in coupling strength among the different structures in a single sample; this was found both in our case and in previous measurements.^{18,34} The result also indicates that precise control over the nanoscale structure will be required in coupled plasmon-emitter systems, which exhibit Fano interference or Rabi splitting. If this control in fabrication can be achieved, then systems can be developed into active devices; for example, a low-power control field can saturate the QD transition, turning off Fano interference or Rabi splitting,^{8,9,109} and enabling nanoscale optical modulation and quantum gates. Our results thus represent an important step towards single-photon nonlinearities and quantum-optical interfaces¹¹⁰ at the nanometer scale and at room temperature.

Chapter 5: Strong coupling between gap plasmon (gold tip) and single quantum dots

5.1 My contribution

This chapter is adapted from a manuscript that has been submitted for review, based on work in collaboration with the group of Dr. Raschke at the University of Colorado. After reading the Nature article from Dr. Baumberg's group about strong coupling in 2016, we started to look for structures that can couple a single QD to gap plasmons. As well as the approach described in the previous chapter, we found that the gold tip used in Dr. Raschke's group for scanning-probe measurements might be the perfect tool to probe the strong coupling between a single QD and a gap plasmon. For these experiments, QDs were deposited on a gold film, and a movable gold tip formed the gap plasmon with the gold film.

Besides the movable gold tip, we needed to precisely control the distance between the QD and the tip. From our previous collaboration with Dr. Gougousi's group, I knew that they could grow sub-nanometer dielectric spacers on top of the QD and the gold film, which could be used to define the distance between the QD and the tip. We found that the alumina film grown by ALD was very effective in controlling the distance between the QD and the gold tip, and also protected the QDs from degradation.

In this project, I prepared the gold film using thermal evaporation and template stripping. Jaron Kropp, a graduate student from Dr. Gougousi's group, deposited a spacer layer using ALD. After the first round of ALD, I deposited the QD with various densities on the substrate. Then, another capping layer was grown by ALD. I also performed numerical calculation to support the measurements. I fitted the photoluminescence spectra using an analytical model to calculate the coupling strength of the coupling.

5.2 Introduction

Optical cavities can enhance and control light-matter interactions by modifying the local electromagnetic density of states of a quantum emitter. In the nanoscale extension, with the manipulation of quantum emitters via plasmonic cavities in the strong coupling regime, this opens new pathways from optoelectronics to quantum information science. However, conventionally, emitters are placed in static plasmonic cavities which limit the ability to tune the coupling strength or investigate different emitters with the same cavity. Here, we present tip-enhanced strong coupling (TESC) spectroscopy, imaging, and control based on scanning probe microscopy using a plasmonic antenna-tip forming a nano-cavity with the emitter placed on a metallic mirror substrate. We observe PL spectra of single quantum dots (QDs) at room temperature that exhibit strong coupling to gap plasmons with mode splittings up to g \sim 163 meV, and anticrossing in the energy spectra of different single QDs over a detuning range of ~ 100 meV with respect to the plasmonic cavity. In addition, by controlling the tipsample cavity with sub-nm precision, we reversibly tune the coupling strength through the strong-coupling transition. Our approach opens a new regime of nano-cavity quantum electrodynamics with manipulation of the nanoscale quantum light-matter interaction of single emitters at room temperature.

5.3 Results



Figure 65 Schematic of tip-enhanced photoluminescence (TEPL) spectroscopy and energy level diagram for the plasmon and exciton in the weak and strong coupling regime. (a) The strongly confined $|E_z|$ fields in a 0.5 nm dielectric capping layer (Al₂O₃) of a single isolated quantum dot (CdSe/ZnS) with a tilted Au tip induce coupling between the plasmon and exciton. Simulated in-plane (b) and out-of-plane (c) optical field distributions in the plasmonic-cavity shown in (a). (d) Energy diagram for the plasmonic-cavity (red), quantum dot (blue), and upper and lower polariton states (green) with photoluminescence energy in the weak (yellow) and strong (green) coupling regimes. When the coupling exceeds system losses, the split polariton states emerge and the system begins to undergo Rabi oscillations as illustrated above. This data has not been published yet.

As we discussed in the introduction section, strong coupling requires a precise control of the distance between the QD and the plasmonic cavity. In Chapter 4, we discussed the study of QDs linked to GNPs, where the length of linking molecules determines the distance between the QD and the GNP. Those linked QD-GNP complexes are randomly deposited on the Ag film. As a result, a gap plasmon is formed between the Ag film and the GNP, which further increases the coupling between the QD and the GNP. In a similar case, we can deposit the QDs on the metal film, Au for instance. Instead of using the GNP, we can use a gold scanning probe to form the gap plasmon, as shown in Figure 65. Comparing to the linked QD-GNP gap plasmon setup, the scanning probe can enable more systematic study of the strong coupling, because the position of the probe can be carefully controlled. In this study, CdSe/ZnS QDs with an emission wavelength of 665 nm were used. The Au film was prepared by thermal evaporation, upon which a sub-nanometer insulating spacer of Al₂O₃ was grown by ALD. The QDs were then drop casted on the coated Au film, and the density of QDs were carefully controlled to avoid forming aggregates. AFM imaging shows that most of the QDs on the surface were single QDs (see Figure 66). After the QD deposition, another layer of Al₂O₃ was grown on the sample as a capping layer.

The plasmonic Au tips are etched electrochemically.¹¹¹ Tip-scattered TEPL spectra are recorded under continuous-wave excitation (632.8 nm, ≤ 1 mW). The tilted tip (35° with respect to the sample surface) maximizes the field enhancement as shown recently.¹¹² In the resulting plasmonic cavity, the corresponding SPP mode is most strongly bound in $|E_z|$ as confirmed by finite-difference time domain (FDTD) simulations (Figure 65). Sample scanning and tip-sample distance is controlled with ~0.2 nm precision using shear-force feedback. All experiments are performed at room temperature.



Figure 66 AFM image of quantum dots on Au substrate. The well-dispersed quantum dots have an average height of 8.0 nm \pm 0.9 nm.

It was found that a very thin Al₂O₃ layer of 0.5 nm gave the best result, as shown in Figure 67. The gap plasmon resonance energy and the QD emission energy overlap well with the 0.5 nm Al₂O₃ layer. The PL spectra show two peaks, as a result of strong coupling. In order to differentiate this two-peak feature from anything else other than strong coupling, a series of controlled measurements were conducted. First, the twopeak feature reduced to one-peak QD PL when the gold tip was pulled away from the QD along the sample surface, as shown in Figure 68. This change in the PL spectra can be explained as due to a decrease in the coupling strength as the gold tip moves away from the QD. The coupling between the QD and the cavity is mediated by the electromagnetic field. When the tip is on top of the QD, the electromagnetic field is the strongest. As the tip moves away, the field intensity decreases. Second, a similar effect can also be seen as the tip moves up, perpendicular to the gold film. These results are strong evidence showing that strong coupling between plasmonic cavity and a single QD is feasible.



Figure 67 Probing tip-enhanced plexciton photoluminescence at room temperature in the strong coupling regime. (a) photoluminescence spectra of the gap plasmon (red), QD exciton (blue), the weakly coupled plasmon-exciton mode (orange), and the strongly coupled plexciton mode (green). (b) photoluminescence evolution of the uncoupled (top) and the strongly coupled (bottom) single QD. (c) TEPL spectra of different single QDs exhibiting variation in coupling strength. (d) Finite element method (FEM) simulation of scattering spectra for the plasmonic-cavity without QD (red) and with a single QD (green). In (a), (c), and (d), the dots and lines indicate the measurement (or simulation) data and the corresponding model fit, respectively.



Figure 68 Active control of tip-induced strong coupling to single quantum dots. (a)Tip-enhanced plexciton photoluminescence for incident light polarization parallel (green) and perpendicular (red) to the tip. (b) 3D finite-difference time domain (FDTD) simulation of the out-of-plane optical field enhancement under experimental conditions of (a). TEPL spectra as the lateral (c) and vertical (d) tip-QD distance is varied from 30 nm to 0 nm and from 0 nm to 4 nm, respectively. The black dots in (c) and (d) indicate the mode energies derived from model fit.

Given the results, researchers who are familiar with this field may argue that the two-peak feature could be a result of multi-exciton emission. In our measurement, we found that it is very easy to see multi-exciton emission if you increase the laser intensity to 0.38 mW with a 0.9 NA 100x objective. However, in these multi-exciton measurements, the spectra look different from what was seen in the tip enhanced photoluminescence measurements. In the multi-exciton photoluminescence measurements, instead of two narrow peaks, we observe one main peak and a broad shoulder on the blue side. This broad shoulder grows with the laser intensity, until the QD is oxidized or damaged.

Another question is how we can be sure that the measured PL is from single QDs, rather than clusters of QDs. To be honest, this is a very difficult question. We can answer it from a theoretical point of view: the mode volume is so small that only one QD will be coupled to the gap plasmon, as shown in Figure 68 b. The best way to tell a single QD from ensemble is to do an autocorrelation measurement. Basically, in an autocorrelation measurement we measure the probability of emitting more than one photon right after the laser excitation pulse. Usually, a single QD will not emit more than one photon right after the excitation pulse. The single QD will remain excited in the very short period after laser excitation, and does not have time to emit and absorb another photon. When multiple QDs are present, multiple photons will be absorbed by the QDs, and then multiple photons will be emitted. However, under strong excitation and laser illumination, more than one exciton can be excited inside one QD, so more photons can also be emitted.¹¹³ Enhancement of radiative recombination rates in the QD by the plasmonic cavity means that emission from multi-exciton states can be efficient, so that autocorrelation measurements may not be effective in these cases to distinguish single QDs from clusters.

5.4 Conclusion

These results are unequivocal evidence of single-QD strong coupling to plasmons. This experiment may thus be the best way to study strong coupling between plasmonic cavity and a single QD. More measurements can be done; for example, a laser power dependent measurement will be interesting. This result can shed some light into the future development of room-temperature strong-coupling applications.^{114–118} On the

other hand, the disadvantage of this measurement is the limited possibility for applications: it will be difficult to make a device using delicate scanning tips.

Chapter 6: Dramatic Modification of Coupled-Plasmon Resonances Following Exposure to Electron Beams

6.1 My contribution

In 2014, we started to work with Dr. Daniel's group to fabricate the sample needed for our strong-coupling study. Brian Szychowski from Dr. Daniel's group tried to link QDs to GNRs, which would lead to making the desired GNR-QD-GNR trimer. At the time, Brian used a scanning electron microscope (SEM) in the UMBC NanoImaging Facility to characterize the synthesized samples. He found it difficult to see the CdSe QDs in the SEM due to the low contrast of CdS as compared to gold. We therefore decided to first work on the synthesis of GNR-GNP-GNR assemblies instead of GNR-QD-GNR assemblies. In the GNR-GNP-GNR synthesis, Brian coated small GNPs with the same capping molecules as used to coat QDs, so the chemistry was the same for QDs and small GNPs; however, GNPs had much higher contrast in SEM, simplifying imaging of the assembled structures. In the end, Brian was able to link small GNPs to the ends of GNRs very consistently.

During my literature research, I found it was interesting to study the interaction between a GNP and a GNR with a short separation. Some groups reported effects of quantum-mechanical tunneling of plasmons between a metal nanoparticles with subnanometer gaps. After studying the sample closely in measurements and simulation, I found that some of the earlier reported experimental data on GNP-GNR structures may be a result of the carbon contamination in SEM imaging. In this study, I made the measurements using an optical/SEM correlated measurement method. I also performed FEM simulations to support the experiments.

6.2 Introduction

We worked with our collaborators to explore the possibilities of positioning nanoparticles using chemical linking processes. Our collaborators started by linking small GNPs to GNRs, because GNPs are much easier to image in an SEM than QDs. We believe the process of linking small GNPs should also apply to linking QDs, because they can be coated with the same capping molecules.

The synthesis process can be found in Figure 69, where a very short molecule is used to link the GNP and the GNR. Because of this short distance between two plasmonic objects (GNP and GNR), we think this is a perfect platform to study potential quantum effects in coupled plasmonic metal nanoparticle systems. It is believed that the oscillating electrons can tunnel through gaps around 0.4 nm or smaller, leading to significant changes in the scattering spectra. In our study, we did not see any such change at such a short particle separation. We also found that the spectral changes, reported by others in this field, could be a result of carbon contamination in SEM imaging, as shown in Figure 69.

The spectral changes that we observe are due to the thin, partially conductive carbonaceous layer that deposits onto the particles during imaging. These changes are particularly significant for coupled nanoparticles with sub-nanometer interparticle gaps, but have largely been neglected in previous studies of such structures, including studies intended to probe quantum-mechanical effects in plasmon coupling. Accounting for the effects of the carbonaceous layer will lead to a more accurate understanding of such systems.

6.3 Results



Figure 69 (a) Schematic of the selective linking of gold nanospheres capped with dithiothreitol (DTT) to the ends of gold nanorods capped with cetyl trimethylammonium bromide (CTAB). (b) A colorized high-resolution transmission-electron microscope image of a linked nanorod-nanosphere dimer. The scale bar is 20 nm. (c) Schematic of the experimental measurements. Dark-field scattering spectra are measured from individual nanorod-nanosphere dimers before and after imaging by scanning transmission electron microscopy (STEM) in a scanning electron microscope.

For this study, nanorods and nanospheres are synthesized following literature procedures.^{119–121} The gold nanorod-nanosphere dimers are prepared, as illustrated in Figure 69, by mixing dithiothreitol (DTT)-capped gold nanospheres with cetyl trimethylammonium bromide (CTAB)-coated gold nanorods. The exposed thiol group at the end of the DTT capping molecules displaces the CTAB molecules at the surface of the nanorods, linking the two particles together. Because the CTAB molecules are more readily displaced from the ends of the rods than from the sides, the spheres preferentially bind to the ends of the rods, as shown for a representative dimer in Figure

69. By using a short crosslinking molecule, we were able to obtain sub-nanometer gaps between the nanorods and nanospheres, resulting in larger coupling strengths than in previous studies. The nanorod-nanosphere assemblies were deposited at low density on a silicon-nitride membrane, and the scattering spectra of individual assemblies are measured in a dark-field microscope. (See Figure 69.) The same assemblies were located and imaged in an SEM operating in scanning transmission electron microscopy (STEM) mode. The samples were then returned to the optical microscope for comparison of their scattering spectra before and after SEM imaging.



Figure 70 Changes in optical-scattering spectra for a gold nanorod-nanosphere dimer due to imaging by scanning transmission electron microscopy (STEM). This dimer was plasma cleaned

prior to STEM imaging. (a-b) Scattering spectra from the dimer before (a) and after (b) STEM imaging. The three spectra (blue, green, and red) are for different polarization angles of the scattered light. Solid lines are measured spectra, and dashed lines are the results of finite-element simulations. The simulations are based on a gap of 0.6 nm between the particles and a carbonaceous shell with thickness of 1 nm after STEM imaging. The energies of coupled modes are shown with dotted vertical lines; ``D" labels the mode with a dipolar resonance in the nanorod, and ``Q" labels the mode with a quadrupolar resonance in the nanorod, and ``Q" labels the mode with a quadrupolar resonance in the nanorod. (c) STEM image of the measured dimer. The colored arrows show the polarization directions for the scattering measurements. Blue, green and red represent -40, 0 and 40 degrees, respectively. (d-g) Simulated charge distributions for the modes indicated in (a-b), for polarization along the direction of the green arrow, (d-e) before STEM, and (f-g) after STEM. Red represents positive charge, and blue represents negative charge. Arrows represent the magnitude and direction of the net dipole moment in each nanoparticle.

Results for a representative dimer are shown in Figure 70. The scattering spectrum before SEM imaging has a dominant low-energy peak and a smaller highenergy feature, whose relative magnitude is sensitive to the polarization of the scattered light. This line shape has previously been attributed to Fano interference between two coupled modes in the system: (1) a bright mode consisting of a dipole mode in the nanorod coupled to a dipole mode in the nanosphere, and (2) a dark mode consisting of a quadrupole mode in the nanorod coupled to a dipole mode of a dipole mode in the nanorod coupled to a dipole mode in the nanosphere, and (2) a dark mode consisting of a quadrupole mode in the nanorod coupled to a dipole mode in the nanosphere.¹²² In order to verify this attribution, we performed FEM simulations of the scattering spectra. The simulated and measured spectra are in good quantitative agreement, as shown in Figure 70. The calculated charge distributions at the energies of the two features support the interpretation of the lower-energy coupled mode as involving a dipolar mode in the nanorod, and the higher-energy mode as involving a quadrupolar mode in the nanorod, as shown in Figure 70. We therefore label the lower-energy mode as "D" and the higher-energy mode as "Q." The D mode also involves a dipolar mode in the nanosphere; this mode dominates for the polarization direction along the line connecting the two particles. Examination of the charge distribution at different energies across the Q mode indicate that involves coupling to both dipolar and quadrupolar modes in the nanosphere. The two resulting coupled modes are separated by a small energy difference, less than the linewidth of each mode. They therefore contribute to a single Fano feature, which is visible for polarizations orthogonal to the line connecting the particles.

After the STEM imaging, the scattering spectra of the same dimer changes dramatically. The high-energy peak takes over and becomes the dominant feature. Both peaks broaden and shift to lower energies. The most likely mechanism for these changes is hydrocarbon contamination, a well-known and unavoidable issue in electron microscopy.^{123–125} The hypothesis that contamination takes place is supported by examining particles, after they have been exposed to high electron doses in the SEM, using high-resolution TEM: amorphous layers are visible on the nanoparticle surfaces.

In order to determine whether this contamination is responsible for the observed changes in the scattering spectrum, we assume that the electron beam deposits a thin carbonaceous layer on the nanoparticle assembly. The exact optical properties of this layer are unknown, but we assume that they are similar to the properties of hydrogenated amorphous carbon (a-C:H) layers that are produced by plasma-enhanced chemical vapor deposition (PECVD).¹²⁶ The optical properties of a-C:H depend on the conditions under which it is deposited, because of changes in the sp³:sp² binding ratio

in the material.^{127–129} We select the dielectric function for a-C:H from Ref. ¹²⁷ that provides the best agreement with our measured scattering spectra. As can be seen in Figure 70a-b, good qualitative agreement is obtained, although some quantitative discrepancies remain; this is not surprising, because the optical properties of carbonaceous layers deposited in an SEM are unlikely to be identical to those of PECVD-deposited a-C:H.

Nonetheless, the reasonable agreement between experiment and calculations strongly supports the interpretation that the dramatic changes in the scattering spectra are due to electron-beam-induced contamination in the SEM. The redshift of the peaks and the change in coupling strength can be understood qualitatively by treating the carbonaceous layer as a purely dielectric shell, as has been done previously when considering electron-beam effects in electron-energy loss spectroscopy (EELS) of silver nanoparticles.¹³⁰ However, the broadening of the peaks and the change in their relative magnitudes cannot be understood without considering the imaginary component of the permittivity of the layer. This imaginary component is related to the conductivity of the carbonaceous material, indicating that electron-beam effects modify coupled-plasmon spectra in ways similar to other, deliberately introduced conductive layers.¹³¹

Another representative result is shown in Figure 71. In this case, the nanosphere is more closely aligned with the long axis of the rod. This results in the optical response before electron-beam exposure being almost entirely dominated by the D mode, with only a weak high-energy shoulder from the Q mode. After electron-beam exposure, the

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relative contribution of the Q mode becomes much stronger. The same model is used for the carbonaceous layer in this case as in Figure 71, and again provides good agreement with the measured spectra, apart from a difference in the position and height of the low-energy peak. The exact way in which the SEM imaging modifies the scattering spectrum of the nanorod-nanosphere dimer is thus seen to depend on the exact arrangement of the particles and the plasmon modes that are involved, but substantial and qualitatively similar changes are observed in both cases. Several other GNR-GNP pairs were measured, and all showed spectral changes that can be understood as resulting from deposition of a partially conductive carbonaceous layer. These changes were not consistent with other potential forms of electron-beam damage, such as migration or sintering of the particles.^{132–138}



Figure 71 Changes in optical-scattering spectra for a gold nanorod-nanosphere dimer due to imaging by scanning transmission electron microscopy (STEM). This dimer was plasma cleaned prior to STEM imaging. (a-b) Scattering spectra from the dimer before (a) and after (b) STEM imaging. The three spectra (blue, green, and red) are for different polarization angles of the scattered light. Solid lines are measured spectra, and dashed lines are the results of finite-element simulations. The simulations are based on a gap of 0.6 nm between the particles and a carbonaceous shell with thickness of 1 nm after STEM imaging. The energies of coupled modes are shown with dotted vertical lines; "D" labels the mode with a dipolar resonance in the nanorod, and "Q" labels the mode with a quadrupolar resonance in the nanorod. (c) STEM image of the measured dimer. The colored arrows show the polarization directions for the scattering measurements. Blue, green and red represent -40, 0 and 40 degrees, respectively. (d-g) Simulated charge distributions for the modes indicated in (a-b), for polarization along the direction of the green arrow, (d-e) before STEM, and (f-g) after STEM. Red

represents positive charge, and blue represents negative charge. Arrows represent the magnitude and direction of the net dipole moment in each nanoparticle.

In order to provide further verification that the electron-induced changes in scattering spectra are due to deposition of a contamination layer, we performed similar measurements on individual GNRs (not linked to any other particle). As shown in Figure 72, the scattering spectrum of a single nanorod shows a large peak due to the longitudinal plasmon resonance; after STEM imaging, this peak shifts to lower energy. We model the change in the nanorod scattering spectrum using the same a-C:H layer as for the coupled nanoparticles, and obtain good quantitative agreement with the measured spectra, as shown in Figure 72. Exposure to a higher electron dose in the SEM leads to a greater redshift, as would be expected for the deposition of a thicker carbonaceous layer. The amount of the redshift is reproducible for a given electron dose across a number of different particles, as shown in Figure 72. The redshifts are also stable: no change is seen in the scattering spectra after the samples have been left in ambient conditions for a week. Only the rods that have been imaged at high magnification exhibit the redshift; other rods on the substrate that were in the SEM only a few microns away from the imaged rods show no red shift.


Figure 72 (a) Scattering spectra for a representative nanorod. Blue lines are before STEM imaging, and red lines are after STEM imaging. Solid lines are measured spectra, and dashed lines are the results of finite-element simulations. A 2-nm α -C:H layer is used in the simulation of the particle after STEM imaging. (b) Peak positions for the scattering spectra from nine individual gold nanorods after three consecutive exposures to the electron beam. Points corresponding to the same individual particles are connected by dashed lines. Electron dose is normalized to the dose from the first exposure.

These interpretation difficulties can be avoided in correlated electron microscope / optical spectroscopy measurements by performing the optical measurements first, before the particles are exposed to electron beams. However, in experiments where the electron beam itself is used for plasmon spectroscopy, such as cathodoluminescence^{139,140} and electron energy loss spectroscopy (EELS),^{130,141} the electron beam-induced effects are unavoidable. Previous studies on isolated particles have suggested that the effects of electron-beam-induced contamination can be neglected under appropriate measurement conditions;¹³⁰ however, we have shown that the spectra of coupled particles are much more sensitive to these effects, and it is unlikely that they can be ignored under any conditions.

This finding presents a particular issue for EELS measurements of tunneling effects in plasmon coupling at the sub-nanometer scale.^{132–134,142,143} Optical-frequency tunneling has an effect on the coupled-plasmon resonances similar to the introduction of a partially conductive medium between the particles.¹⁴⁴ Modeling of these experiments, however, has generally not included the presence of the carbonaceous contamination layer, which is itself partially conductive. In other words, electron-beam contamination has the potential to mimic quantum plasmonic effects and should be carefully considered when interpreting experimental results. For the experiments reported here, a purely classical model that includes the carbonaceous layer quantitatively explains the spectra of coupled particles with an interparticle spacing of 0.6 nm, indicating that quantum-mechanical effects are insignificant at this separation.



Figure 73 Scattering and photoluminescence of the same single gold nanorod.

In the course of these measurements, I noticed that GNRs exhibited consideratble PL under laser illumination, unlike bulk gold. Similar PL from GNRs has been reported recently.^{103,145–147} Two different mechanisms for this PL were proposed: an electronic Raman scattering process,¹⁰³ and a Purcell enhanced hot carrier emission process.¹⁴⁶ The details of those two mechanisms are beyond this thesis. It was

interesting to note that the PL resonance is the same as the scattering resonance due to plasmons in the GNR. This provides an alternative method to characterize the plasmon resonances of GNRs, particularly smaller GNRs for which scattering cross-sections are small. In particular, using our dark-field setup, it was almost impossible to measure the scattering of a particle smaller than 50 nm (or a rod of 20 nm by 40 nm) because of the scattering intensity scales with a^6 , and a is the size of a gold nanoparticle. However, the PL spectrum of these GNRs still had a reasonable signal-to-noise ratio even for small gold nanoparticles, as shown in Figure 74. More studies can be done on this topic. It would be interesting to see how the PL signal-to-noise ratio depends on laser polarization, power, wavelength, and pulse duration. From a practical point of view, the PL measurement is easier than the dark-field measurement in terms of alignment and sample preparation. The disadvantage is that under strong laser illumination the gold nanorod might be damaged.



Figure 74 Signal to noise ratio of several single gold nanorods in photoluminescence and scattering mesasurements. I saw a much larger variance in the scattering signal-to-noise raito compared to the photoluminescence measurement.

6.4 Conclusion

In summary, we have observed strong, qualitative changes in the optical scattering spectra of asymmetrical dimers of plasmonic metal nanoparticles after electron microscope imaging. We were able to explain the results by assuming that the electron beam causes the deposition of an amorphous hydrogenated carbon layer. Our results suggested that the effects of the electron beam can be mitigated but not eliminated, so that any study of coupled-plasmon resonances should take these effects into account. In particular, when performing correlated electron microscope imaging and optical spectroscopy, the optical measurements should be performed first; when performing cathodoluminescence and EELS, carbonaceous contamination should be included in the models used. This is of particular importance when investigating quantum

mechanical effects in plasmon coupling, because the spectral changes that we report here are qualitatively similar to the changes that are the result of interparticle tunneling. Another important factor in these measurements is the linking molecule. The electric property of the molecules should also play a very important role in the electron tunneling between the GNP and GNR.

Future work will be dedicated to determining whether the deposited layers can be removed without damaging the plasmonic metal nanostructures, either through more aggressive plasma cleaning or by chemical methods.¹⁴⁸ Our study also raises the possibility of selectively engineering the spectra of individual metal nanostructures post-synthesis by deliberately exposing them to electron beams. This has the potential to provide control over plasmon coupling similar to other approaches that use electrochemical methods,^{131,149} physical methods,^{150,151} or the infiltration of water,¹⁵² but with the advantage that individual assemblies can be addressed and tuned separately, without making changes to other assemblies only microns away. Further control may be possible by using electron beams to deliberately deposit more complex materials onto the linked particles.¹⁵³

Chapter 7: Electron Transfer from Single Semiconductor Nanocrystals to Individual Acceptor Molecules

7.1 My contribution

In early 2015, I started to take measurements of samples prepared by Dr. Amin from Dr. Weiss' group. The time-resolved single QD photoluminescence measurement method used in this study was very helpful to the measurements I implemented from 2016 to 2018. James Loy, one of the undergraduate students in our group, made a LabVIEW program to control the motion stages. Later, I made changes to the program to perform optical / SEM correlated microscopy.

In this study, I attached viologen molecules onto the surfaces of the QD to form an assembly, which led to electron transfer from the QD to the molecules. In order to understand the physics, I measured the electron transfer rate. Our measurements were able to resolve transfer rates at the level of single electrons moving from individual QDs to single molecules on their surfaces.

7.2 Introduction

This study focuses on the measurement of photoinduced electron-transfer from individual CdSe/CdS QDs to methyl viologen acceptor molecules adsorbed on the QD surfaces, using time-resolved PL at the single-nanocrystal level. For each QD measured, the electron-transfer rate is constant over time, and the PL blinking dynamics are independent of the measured transfer rate. The total electron-transfer rate is

distributed in discrete, constant increments, corresponding to discrete numbers of adsorbed molecules on each QD. The results thus validate previous assumptions that viologen molecules adsorb independently on QD surfaces and that the total electrontransfer rate from a single QD to multiple molecules on its surface is simply the sum of the transfer rates to the individual molecules. The measurement provides an optical method to count the number of active acceptor molecules bound to a single nanocrystal, and opens up new possibilities for mechanistic studies of charge transfer at the nanoscale.



Figure 75 (a) Transmission-electron-microscope (TEM) image of CdS/CdS core-shell quantum dots (QDs). (b) Absorption (green) and emission (red) spectra of the QD ensemble in chloroform solution.

(c) Emission spectra for a single QD (green) and a cluster of QDs (red). (d): Time-resolved photoluminescence from a single QD.

7.3 Results

The core/shell QDs were synthesized using modifications of published procedures.^{154,155} The resulting nanoparticles have a quasi-spherical CdSe core and an approximately tetrahedral CdS shell, as shown in Figure 75a. The core radius is approximately 1.6 nm, and the shell thickness varies between 4 and 5 monolayers. The lowest-energy absorption peak from the QDs occurs at a wavelength of 631 nm, and the emission peak is centered at 649 nm, as shown in Figure 75b. After the QDs were synthesized, we adsorbed methyl viologen molecules on their surfaces. These molecules were selected because they have been well established by ensemble measurements as electron acceptors for CdSe QDs and CdS QDs.^{156–163} The adsorption procedure was designed so that a small number of viologen molecules are adsorbed on each QD, and so that aggregation of QDs in solution is minimized. The QD-viologen complexes were then deposited on a glass coverslip at low density, so that individual complexes can be resolved in a far-field optical microscope.

Single QDs on the coverslip surface were distinguished from small aggregates or clusters of QDs by measuring the linewidths of their PL spectra, as shown in Figure 75c: a single QD has a narrow linewidth of approximately 18 nm or less, whereas a cluster has a broader spectrum, due to differences in the sizes of the QDs making up the cluster. Figure 75c shows an example; the cluster also shows an asymmetric, flattopped spectrum, due to the contribution of several individual QD spectra that is qualitatively different from the single-QD spectrum. In addition, we assume that any points exhibiting unusually bright photoluminescence or not undergoing blinking (fluorescence intermittency) are clusters rather than individual QDs.

Once a single QD has been identified, its photoluminescence is resolved in time using time-correlated single-photon counting (TCSPC). The arrival time of each detected photon is recorded relative to the corresponding excitation laser pulse and relative to the start of the experiment. A histogram of the delay times between excitation and emission gives the time-averaged PL kinetics for the QD. As shown in Figure 75d, this total curve includes a tail at long delay times, with a time constant greater than 100 ns; this may be due to a "delayed emission" process, in which carriers are trapped on surface states for a certain amount of time before returning to the core of the quantum dot and recombining to emit a photon.^{164,165}

Even at times shorter than this slow decay tail, the time-averaged decay dynamics are still not described by a single exponential, either for QDs or QD-viologen complexes. At least part of this can be attributed to fluorescence intermittency, or blinking, of the QD, with corresponding fluctuations in the non-radiative emission rate.¹⁶⁶ However, some previous studies have interpreted single-QD data as providing evidence that photoinduced charge-transfer rates also fluctuate over time.^{167–170} In order to determine whether this fluctuation is occurring in our samples, we divide each measurement into a series of time bins. For each bin, we generate a histogram similar to Figure 75d, only with many fewer photons. We then fit this histogram to a single exponential function to get the decay rate. In order to obtain reasonable time resolution over the experiment, the number of photons in each bin must be limited; however, the

uncertainty in the lifetime increases as the number of photons in the bin decreases. We ensure that this lifetime uncertainty remains constant over the duration of the experiment and from one QD to another by adjusting the bin size so that each bin has 350 photons. We also calculate the average intensity in each bin by dividing 350 by the difference between the arrival times of the first and last photons in the bin.

Figure 76 shows the distributions of intensities and decay rates obtained in this way for five individual QDs. Because the QDs that we study have suppressed blinking compared to conventional QDs, the distributions are dominated by the properties of the bright, emissive state of the QD. The average intensity for a particular QD depends on the efficiency with which emitted photons are collected, which in turn is sensitive to the precise alignment of the QD relative to the focus of the microscope objective and the orientation of the QD on the surface; it is thus not meaningful to compare absolute intensities from one QD to another. It is clear, however, that the relative standard deviations in the intensity and in the decay rate is constant from one QD to another, even as the average decay rate increases by a factor of approximately 2.5. These standard deviations are most likely dominated by statistical error due to the finite number of photons in each bin. We thus do not observe the dynamic heterogeneity that has been claimed in previous studies. This may be because previous studies employed different acceptor molecules, but it may also be due to the use of bins with constant time duration in the previous studies: for QDs with adsorbed acceptor molecules, the average photon detection rate is lower than it is for QDs without adsorbed molecules, so the fitting error increases when constant-duration bins are used. The apparent broadening of the lifetime distribution for QDs undergoing charge transfer in previous studies may thus simply be a statistical artifact.



Figure 76 (a) Joint distribution of photoluminescence intensity (in thousands of counts per second, kcps) and decay rate for five individual QDs with viologen molecules adsorbed on their surfaces. The measurement is divided into time bins, each with 350 detected photons, and the average intensity and decay rate are determined for each time bin. The color scale represents the number of time bins with a given intensity and decay rate, normalized by the maximum number. (b) Distribution of decay rates, determined as in (a). Blue points are experimental data and red lines are fits to Gaussian functions. The mean decay rates for the five QDs, from top to bottom, are 0.028, 0.042, 0.047, 0.061, and 0.072 ns-1, respectively. The corresponding standard deviations in the decay rates are 0.013, 0.014, 0.013, 0.016, and 0.015 ns-1, respectively.

For our measurements, the absence of broadening in the lifetime distribution means that we can assign to each QD a single average decay rate, which corresponds to the sum of the rate at which excitons in the QD recombine and the charge-transfer rate for that QD. In order to quantitatively account for the recombination rate, we must take into account the fluctuating non-radiative recombination rate associated with blinking. Before doing so, we examine the blinking itself in order to determine whether its statistical properties are affected by the charge-transfer process.



Figure 77 (a) Blinking time distributions for the bright state obtained by combining the data from several individual QDs. The QDs are sorted into three groups according to their average decay rates: groups 0 to 3 correspond to approximate decay rates of 0.03, 0.04, 0.05 and 0.06 ns-1, respectively. The distributions all follow truncated power-law distributions with exponents, α_{on} , of -1.5 and truncation times, $\Gamma_{-}(on)$, of 0.2, 0.2, 0.3, and 0.3 s-1, respectively. (b) Blinking time distributions for the dark state obtained by combining the data from several individual QDs. The distributions all follow power-law distributions; the corresponding exponents, α off, are -2.1, -2.1, -2.3, and -2.0, respectively.

Blinking statistics are most commonly described in terms of the distributions of times spent in the bright and dark states; results are shown for our samples in Figure

77.¹⁷¹ In this figure, the QDs are grouped according to their mean decay rates, and the statistics from all the QDs in each group are combined. The distributions for the dark states follow a power law, $\rho(t) = t^{-\alpha_{off/on}}$, with α_{off} =-2.1 ± 0.1 for all of the groups, consistent with values previously reported for similar CdSe/CdS core/shell QDs.¹⁵⁴ The distribution for the bright states is fitted with a truncated power law distribution:^{49,172}

$$P(t) = A * t^{-\alpha_{on}} \exp(-\Gamma_{on} t).$$
(34)

Both the truncation time, Γ_{on} , and the power-law exponent, α_{on} , are found to be constant across the four groups, even though group 0 is not undergoing electron transfer, and groups 1 – 3 are all undergoing electron transfer at different rates. Our results thus indicate that the electron-transfer process does not affect the blinking statistics. This result again contrasts previous reports of modified blinking statistics in the presence of photoinduced charge transfer.^{173–175} Similar to our observation of the absence of dynamic heterogeneity in photoinduced electron-transfer rates, our observation of unmodified blinking statistics may be due to the particular QD-molecule system studied, or it may reflect statistical artifacts in previous analyses.

Taking the results for QD blinking together with the results for the single-QD lifetime distributions, we conclude that the only effect of viologen molecules on the QD surfaces is to increase the decay rate by a certain amount, with that amount being fixed for each individual QD observed. The total decay rate includes radiative decay, electron transfer, and a fluctuating non-radiative decay.¹⁶⁶ The contribution of non-radiative decay, however, can be eliminated by analyzing only photons collected when the QD is in its bright state.^{50,176} The histogram of decay times for only these photons is a single exponential for delay times between 3.5 ns and 30 ns for all of the QDs

studied. There is a fast decay at delay times less than ~3.5 ns, most likely due to scattered laser light and charge trapping in the QD. At delay times longer than about 30 ns, the signal is dominated by shot noise. The CdS shell thickness for the core / shell QDs we use is such that the electron transfer process is expected to occur between these two limiting time scales.¹⁷³ We can thus determine the decay time by fitting the histogram to a single exponential for delay times between 3.5 ns and 30 ns.

Figure 78 shows distributions of decay rates determined in this way for a series of individual QDs from three separately prepared samples. Figure 78(a1) shows results for a number of QDs from a sample that was not treated with viologen molecules. These QDs show an average decay rate of 0.029 ns⁻¹, with a standard deviation of approximately 0.003 ns⁻¹. Figure 78 (b1) and (c1) show results for a number of QDs from two different, separately prepared samples of QDs with viologen molecules adsorbed randomly on their surfaces. For both collections of QDs, there is a peak with the same average decay rate as the viologen-free dots, and there are a series of evenlyspaced peaks with higher decay rates. We can thus attribute each peak to a discrete number of viologens on each QD; i.e., the lowest-rate peak corresponds to no adsorbed molecules, the next peak to one adsorbed molecule, the next peak to two adsorbed molecules, and so on. The even spacing of the peaks indicates that electron transfer to each viologen molecule is independent from electron transfer to the others, so that the total electron-transfer rate is simply the sum of the individual electron-transfer rates. In other words, the decay rate for each QD is given by

$$\gamma = n \times \gamma_{CT,int} + \gamma_0 \tag{35}$$

where γ_0 is the decay rate of an exciton in a QD without any viologen molecules attached; $\gamma_{CT,int}$ is the photoinduced electron transfer rate from the QD to a single viologen molecule (the intrinsic charge-transfer rate); and n is the number of viologen molecules absorbed on a given QD. This is consistent with previous ensemble measurements, where the electron transfer rate was observed to be linear in the number of adsorbed electron acceptors.¹⁵⁶



Figure 78 (a) Distribution of decay rates for 20 individual QDs with no adsorbed viologen molecules. The results correspond to the distribution of radiative recombination rates in the quantum-dot sample. The bars are experimental data, and the points are a Gaussian fit with a center at 0.029 ns⁻¹ and a width of 0.003 ns⁻¹. (b1, c1) Distribution of decay rates for 29 and 62 QDs, respectively, with adsorbed viologen molecules, from two different, separately prepared samples. The separate peaks correspond to different discrete numbers of viologen molecules on the QD surfaces. The points are simulated distributions using the Gaussian fit from (a), a constant electron-transfer rate of 0.009 ns⁻¹ per molecule, and a Poisson distribution of molecules on the QD surfaces. (b2, c2) Simulated distributions using the raw experimental data from (a), a constant electron-transfer rate of 0.009 ns⁻¹ per molecule, and a Poisson

distribution of molecules on the QD surfaces. Simulated frequency values are rounded to the nearest integer.

If each viologen molecule adsorbs independently onto a given QD, then the number of molecules adsorbed on each QD will follow a binomial distribution.¹⁷⁷ If the average number of viologens bound to each QD is much less than the number of available binding sites, then the binomial distribution is well approximated by a Poisson distribution.^{178,179} The distribution of decay rates is then described by

$$P(\gamma) = \sum_{n=0}^{\infty} \frac{\lambda^n e^{-\lambda}}{n!} \times p_0(\gamma_0 + n \times \gamma_{CT,int})$$
(36)

where $p_0(\gamma_0)$ is the decay-rate distribution for QDs with no viologen molecules and λ is the average number of molecules adsorbed per quantum dot. In order to compare this model to experiment, we can take $p_0(\gamma_0)$ in one of two ways: (1) from a Gaussian fit to the experimentally measured decay-rate distribution for the control group that has not been treated with viologen, or (2) directly from the experimental distribution for this control group. Figure 78 (b1) and (c1) show the modeled distribution obtained using the first method, and Figure 78 (b2) and (c2) show the modeled distribution obtained distributions are obtained for the two collections of QD-viologen complexes by using the same value, γ_A =0.009 ns⁻¹, for the electron-transfer rate from a single QD to a single adsorbed viologen molecule. The only remaining fitting parameter is λ , the average number of viologens per QD; unlike γ_A , this parameter is different for the two collections of QD-viologen complexes.

measured distributions are attributable to statistical variations due to the finite number of QDs measured for each sample.

The measured electron-transfer rate of 0.009 ns⁻¹ from a QD to a single adsorbed viologen molecule is similar to the electron-transfer rate inferred from previous single-dot studies from core/shell QDs with comparable shell thicknesses to adsorbed fluorescein molecules.¹⁷³ The results are thus consistent with the assumption that the total electron-transfer rate for a QD with n molecules on its surface is simply n times the electron-transfer rate to a single molecule; that is, electron transfer to each viologen molecule on the surface of a given QD is independent from electron transfer to the other molecules on the surface of the same QD. Moreover, the electron-transfer rate appears to be the same for all viologen molecules adsorbed on QD surfaces, despite the fact that the shell thickness varies across the surface of each QD. This most likely implies that the difference in electron-transfer rate for molecules adsorbed at different locations is smaller than the natural variation in decay rates among the QDs in the ensemble, so that the variation in electron-transfer rate does not significantly broaden the peaks in the distribution of decay times. In addition, the distribution may be dominated by electron transfer to viologen molecules that are located closest to the QD cores and thus have the fastest transfer rate. This possibility is supported by the fact that the agreement between theory and measurement appears to be somewhat poorer for faster decay rates, suggesting there are more dots observed with fast decay rates than would be expected on the basis of a single intrinsic electron-transfer rate and Poisson statistics for the number of adsorbed molecules.

Determining whether there is any discrepancy between the simple model of Eq. (37) and experiment will require measuring a larger number of QDs from each sample. Currently, this number is limited by the stability the sample: measurements were made over at most two days on a single sample because the viologen molecules appeared to degrade¹⁷⁹ or desorb from the QD surfaces over longer time scales. In order to measure more individual QDs and obtain greater statistical significance, an improvement in sample stability will be required.

As a validation of our single-QD results, we perform time-resolved photoluminescence measurements for the ensemble of QDs in solution. The results are shown in Figure 79, and are fit by assuming a Poisson distribution of viologen molecules on the QDs:¹⁵⁶

$$I(t) = \sum_{n=0}^{\infty} \frac{\lambda^n e^{-\lambda}}{n!} \times I_0(t) \times e^{-n \times \gamma_{CT,int} t}$$
(37)

where I₀ (t) is the decay curve of quantum dots in solution with no viologen molecules (measured experimentally, as shown in Figure 79). A fit using the electron-transfer rate $\gamma_{CT,int}$ = 0.009 ns⁻¹ from the single-dot measurements is in good agreement with the ensemble measurements for delay times from approximately 7 ns to 30 ns; the only free parameter in this fit is λ . For shorter decay times, there is a fast decay that is not fit by the model. This can be attributed to small clusters of QDs in solution,¹⁸⁰ which are known to have fast decays due to energy transfer among the QDs in the clusters. Because the clusters emit more intensely than individual QDs, even a small fraction of clusters can affect the observed ensemble dynamics. In our single-QD measurements,

we can exclude these clusters from the analysis based on their photoluminescence linewidths, intensities, and blinking characteristics; this selectivity is one advantage of the single-particle approach.



Figure 79 Time-resolved photoluminescence for QDs in chloroform solution, in counts per second (cps). Red circles are for QDs alone and blue circles are for QDs with adsorbed viologen molecules. The black dashed line is a fit to the QDs with viologen, using a single-molecule photoinduced electron-transfer rate of 0.009 ns⁻¹ and an average of 1.0 adsorbed viologens per QD.

7.4 Conclusion

In summary, we measured the photoinduced electron transfer rate from individual CdSe/CdS core/shell quantum dots to methyl viologen molecules adsorbed on their surfaces. Each dot exhibits a constant single donor-acceptor transfer rate (0.009 ± 0.003 ns⁻¹). Since this rate exceeds the standard deviation in the excited-state decay rates

among the QDs in the sample, we are able for the first time to resolve the number of acceptor molecules adsorbed on a given QD using the total photoluminescence decay rate of the QD. In other words, we are able to count, through optical measurements, the number of acceptor molecules adsorbed on the surface of a particular QD. This opens up new possibilities for the detection of individual molecules that do not fluoresce and whose optical absorption and scattering cross-sections are too small to allow for direct measurement, with potential applications in biosensing.¹⁸¹ It may also be possible to monitor the adsorption and desorption of individual acceptor molecules from QD surfaces through real-time changes in charge-transfer rates. Using anisotropic nanocrystals, such as core-shell nanorods¹⁸² and nanoplatelets,¹⁸³ will enable studies of how photoinduced electron transfer depends on the spatial location of the acceptor molecule on the nanoparticle surface. Selective excitation of particular transitions in the nanocrystals will enable studies of how photoinduced electron-transfer dynamics interact with charge relaxation and localization dynamics within the nanocrystals.¹⁸⁴ In order to enable these future measurements, it will be necessary to improve the longterm stability of the nanocrystal-acceptor complexes, so that a statistically significant number of complexes can be characterized before the properties of the sample change. It will also be advantageous to synthesize ensembles of nanocrystals with very narrow distributions of radiative decay times, so that changes in dynamics due to electron transfer can easily be distinguished from heterogeneity in the sample. With these improvements, single-QD / single-molecule charge-transfer measurements should provide the mechanistic understanding required to engineer charge-transfer dynamics at the nanoscale, enabling the optimization of applications including photocatalysis and low-cost photovoltaics.

Chapter 8: Conclusion

In my thesis work, I confirmed in experiments that strong coupling exists in a structure that consists of a single QD and a gap plasmon. In addition, our collaborator was able to achieve real-time active control of strong emitter-cavity coupling at the nano-scale.

To recap, I used QDs as emitters and a plasmonic structure as the cavity. As pointed out by many studies in the field, it is hard to achieve strong coupling between single QDs and the plasmonic cavity. To solve this challenge, I used various methods to achieve strong coupling, including a single QD coupled to gap plasmons and a single QD coupling to gold-tip plasmons. In the first method, our collaborator managed to synthesize QD-GNP assemblies and I deposited them on a silver substrate. In this sample, the linked GNP formed a gap plasmon with the silver film. I call this method a hybrid method, compared to pure chemically linked samples or samples fully made in the cleanroom. So far, before any additional improvement of the chemical linking process, this hybrid method seems to be the optimal choice, because the gap-plasmon architecture significantly reduces the difficulty in putting the QD in the "hot spot", and the chemical linking reduces the number of un-coupled QDs in the background. This study should give other researchers some inspirations about the sample preparation to further improve the sample yield.

Another robust method we discovered is the combination of tip-enhanced photoluminescence setup and the gap-plasmon architecture. Through a collaboration among Dr. Pelton's group, Dr. Gougousi's group, and Dr. Raschke's group, we demonstrated one of the first measurements of real-time control of the coupling strength between a single QD and gap plasmons. We showed that the coupling strength also depended on the separation between the gold tip and the QD. This measurement demonstrated that the photoluminescence of a strongly coupled QD-GNP system exhibited the expected two-peak feature. Our studies opened up new possibilities in quantum information and non-linear optics.

Other than showing the possibilities of strong coupling between single QDs and GNPs, I found some issues in the previous studies of other groups. One of the issues was the difficulty in electron imaging, which could lead to contamination of the sample and modifies scattering spectra of the sample. Another issue is that the scattering spectra cannot be used to determine the coupling strength, because of the irregularities in the sample population can result in double-peak scattering spectra even without any emitters. To avoid the ambiguity, I implemented the correlated single particle photoluminescence and scattering measurement to study the strong-coupling effect. In photoluminescence of the gap plasmons should be considered as well. These two effects, including irregularities in scattering and multi-excitons in photoluminescence, could give very similar spectra to the strong coupling spectra, and special care should be given to the interpretation of the measurement data.

In addition, the common optical methods used to test whether a single QD was present could fail when the QD is in the proximity of a plasmonic cavity. For this reason, it was challenging to prove that only one QD was involved in the strong coupling. Even with careful sample preparation and numerical simulations, we still lacked direct confirmation that only one QD was involved in the GNP-QD-silver film study. Finally, optical control of the coupling between single QDs and plasmons turned out to be non-trivial. In order to turn off strong coupling or eliminate the Fanointerference dip, a relatively high-power CW laser source was needed. But, high incident laser power density could lead to non-reversible oxidation of the QD. To resolve this issue, the sample preparation needs to be improved, improving the QD photostability, before any real-world applications will be possible.

Several improvements could be made in our lab in order to further approach practical applications. First, we can make the measurement in an inert gas environment, which will eliminate QD oxidation. Second, we can improve the chemical linking process, and link a QD to two sharpened GNRs. GNRs with sharp ends will induce stronger coupling with the QD. Third, Dr. Raschke's group plans to perform the experiment at a low temperature, which can further improve the quality of the data, because of a lower loss of QDs at a low temperature. Finally, even though the sample yield is low, we can use the ultra-fast laser ablation technology to annihilate the unsuccessful sample on the substrate. An intense laser beam can ablate the material and remove the unwanted structures. In the ultrafast laser micromachining process, materials can be easily removed with a lateral resolution of less than 10 µm.¹⁸⁵ After removing the undesired particles on the metal film, an ensemble of successful structures will be available; an illustration is shown in Figure 80.



Figure 80 Femtosecond laser pulses can ablate material with minimum damage to the surrounding of the laser pulse. In the first step, the sample is scanned to optically characterize the sample. In the second step, the unsuccessful particles are exposed to an intense femtosecond beam, and these particles are removed. In the last step, much higher yield is achieved on a substrate.

Appendices

Procedure for motion control software

In our measurements, we used a home-built LabVIEW program to control the XY stage and the Z focusing stage. The procedures are the following:

1. Home/referencing the XY stage. This step must be done first if the stage is powered off during power outage.



- a. Double click the icon of "SPiiPlus MMI Application Studio 2.20" on the desktop
- b. Make sure the stage is powered up and connected to the control PC
- c. Right click "NTM01690B2" in the workspace of the software, and hit connect
- d. In program manager, right click buffer 2 and run this buffer (MAKE SURE THE OBJECTIVE IS REMOVED, THE XY STAGE WILL MOVE OVER ITS FULL RANGE!!)
- Start the LabVIEW program "Microscopy_Interface_save_Positions_6-3-2016 haixu" on the desktop



- a. Double click the icon to start
- b. Click "run." A screenshot of the software is shown in Figure 81
- c. Select XY-stage and Z-Focus stage by clicking the buttons
- d. Click "ACTIVATE"
- e. In the tab "Stage Control," click "connect", then the XY-stage will be connected
- f. Enable the axes of the stage. The Z-focus stage should be ready as well



Figure 81 Screenshot of the LabVIEW motion control software.

Procedure for photoluminescence microscopy



Figure 82 The photoluminescence setup. 1: 510 nm diode laser, coupled with fiber optics. 2. Fiber coupler exit. 3. Silver mirror. 4. Laser clean up filter, can switch from 510 nm to 420 nm. 5: Silver mirror. 6. Variable ND filter. 7-8: Telescope for 5X beam expansion. 9: Silver mirror. 10: Silver mirror. 11: Removable lens to switch from the focusing mode to defocusing mode. 12: Silver mirror. 13: Dichroic filter. 14: Objective. 15. Two long pass filters. 16: Spectrometer. 17: CCD camera. 18-19: Single photon detector for time-resolved photoluminescence. The light path of the green laser is labeled in green and the emission of the sample is labeled in red.

 In the photoluminescence measurements (Figure 24), we use coherent light source to excite the sample. We have two lasers operating at 420 nm and 510 nm. In the pulsed mode the laser pulse can be as short as 100 ps. The max average power is around 40 mW.

- The 510 nm green laser is bundled with a single mode fiber, which improve the beam quality of the laser. The beam collimator of the fiber is shown in Figure 82 label 2.
- 3. A silver mirror is used to deflect the beam.
- 4. The laser light is further cleaned by the cleanup filter to get rid of the tails in the spectra, which is critical in photoluminescence measurements. The cleanup filter is shown in Figure 82 label 4.
- 5. A silver mirror is used to deflect the beam.
- 6. We use a variable ND filter to adjust the laser power, which is shown in Figure 82 label 6. In the photoluminescence measurements, we tend to keep the current in the diode constant. This current controls the laser intensity, but modifying the current in the diode can also modify the pulse width of the laser, which can affect the measurement.
- 7. The laser beam is expanded from a diameter of 5 mm to 25 mm. The expanded beam can cover the whole back aperture of the objectives. A larger beam diameter at the back aperture of the objective leads to a tighter focal spot.
- 8. Same as 7.
- 9. A silver mirror is used to deflect the beam.
- 10. A silver mirror is used to deflect the beam.
- 11. The laser beam can be modulated by a removable lens in the system, which controls whether the laser beam illuminates a small region on the substrate or a larger region. Without this lens, a collimated aser beam will be focused to a point by the objective. On the other hand, with this lens, the beam is focused

onto the back aperature of the objective, leading to the illumination of a larger area on the sample. This can be used to find particles in a larger area. Once we find a particle to make measurement, we switch to the tightly focused mode, where only the particle of interest will be excited. Because of the design defect from Thorlabs, the dichroic filter is not perfectly centered. As a result, this lens is slightly misaligned on purpose to correct this flaw.

- 12. A silver mirror is used to deflect the beam.
- 13. The dichroic filter (Semrock) can direct laser light into the objective and block the scattered laser light from getting into the spectrometer. We build our system around the Thorlabs "cage" platform. In the "cage" system, everything is concentric. However, Thorlabs did not consider the fact that the dichroic filter has a finite thickness. After the dichroic filter, the reflected laser light is no longer centered. We must add an extra lens (11) to compensate this problem.
- 14. We use Nikon objectives in our system, and 100 X NA 1.4 immersion oil objective is our best choice for the photoluminescence measurement. We found that the immersion oil introduces some surface tension between the objective and the glass substrate. This force can lead to focus drift over time. We found that a stability of around 10 minutes can be achieved by carefully adjusting the Z axis using a Piezo motor stage from Thorlabs. Since the weight of the objective is hanging on the Z stage, the contact point is very important. We found a sapphire contact significantly improves the stability of the Z axis movement. The sample is mounted on a sample holder, which is mounted on the Alio (AI-CM-5000-050-XY) linear stage. This stage has a 5 nm step size.

The encoder of the stage can also report the location of the stage. These locations help us to rebuild the pattern of the particles to do correlated measurements. The collected light passing through the objective should be collimated (Nikon infinity-corrected objective). This light is then focused by a tube lens (200 mm) to form an image.

- 15. The collected light first goes through a 200 mm tube lens to form an image, then two more long-pass filters are used to make sure all the light from the laser has been eliminated.
- 16. At the entrance of the spectrometer, a slit can regulate the light coming into the spectrometer. The spectrometer is equipped with 3 different gratings.
- 17. The spectrometer can be controlled by either the LightField software from Princeton Instruments or the LabView program. When taking a photoluminescence spectrum, the slit will be narrowed to eliminate the particles in the horizontal direction. We can choose a certain number of rows of pixels on the CCD to eliminate the unwanted signal in the vertical direction. Then we will rotate the grating inside the spectrometer to the center wavelength. An exposure of 1 to 20 seconds will be sufficient to form a nice photoluminescence emission spectrum.
- 18. In the time-resolved photoluminescence measurement, a removable mirror will be placed in the light path to direct the light to a single photon detector (MPD model PD-050-CTD). This detector is mounted on a 3-axis stage to align the center of the detector with the particle. The maximum count rate of the detector is 10⁶ counts per second. A physical timing device can use long electrical cables

to shift the timing of the signal. By adjusting the timing, the TCSPC peak can be shifted to 0. The collected TCSPC data can provide information about the dynamics of the excited particle on an ns scale.

19. A single photon detector, which is used to make ensemble TCSPC measurements.

Procedure for dark-field microscopy



Figure 83 The dark-field scattering setup. 1: Halogen lamp. 2: Silver mirror, with a variable aperture. 3: Silver Mirror. 4-5: Telescope used to modify the beam entering the dark-field cube. 5 can be moved in XYZ directions. 6: Dark-filed cube that creates a hollow light ring. 7: Dark-filed objective. 8: Silver mirror. 9: Slit of the spectrometer. 10: Spectrometer. 11: CCD camera. 12: XY motion stage.

- 1. A Halogen lamp from Nikon was used, which has a broad spectrum centered on 650 nm.
- 2. A silver mirror deflects the beam.
- 3. A silver mirror deflects the beam.
- 4. Lens 4 and 5 in Figure 83 are used to adjust the beam divergence coming into the dark-field cube. Nikon did not provide the necessary information about the beam coming into the dark-field cube. As a result, I had to try several different combinations of the lenses to have a decent signal to noise ratio. Further improvement is possible.
- 5. Lens 5 can be adjusted in all three directions for the best alignment.
- The dark-field cube is used to block the center area of the lamp light to create a ring. The cube can be seen in Figure 84.
- A specialized Nikon dark-field objective was used (TU PLAN FLUOR BD 100X).
- 8. A silver mirror deflects the beam, and this mirror can be adjusted to align with the entrance of the spectrometer.
- 9. The collected light first goes through a 200 mm tube lens to form an image. In addition, at the entrance of the spectrometer, a slit can regulate the light coming into the spectrometer. The spectrometer is equipped with 3 different gratings. Furthermore, a half-wave plate and a linear polarizer can be put in front of the slit to take polarization dependent measurements.
- 10. Same as 9.

11. The spectrometer can be controlled by either the LightField software from Princeton Instruments or the LabView program. When taking a photoluminescence spectrum, the slit will be narrowed to eliminate the particles in the horizontal direction. We can choose the certain number of rows of pixels on the CCD to eliminate the unwanted signal in the vertical direction. Then we will rotate the grating inside the spectrometer to the center wavelength. An exposure of 1 to 20 seconds will be sufficient to form a nice scattering spectrum.



Figure 84 Nikon dark-field cube. The light comes in from the lens (top) and exit from the right.

Substrates:

For coverslips, the premium super clean substrate (blue package) from Fisher seems to work fine. It can be used without further cleaning. For glass slides, the cleaning is required. You can use organic solvent, like methanol to rinse it. Then use the commercial "First Contact" cleaner to further clean the sample. You need to take one end of the slides. Apply the cleaner, covering the center part of the slides and part of




Figure 85 Clean the glass slides for dark-field scattering using peel-off method.

The air-dry objective is easy to use and can avoid the need to clean off the objective. The signal to noise ratio is not as good as the immersion oil method with the oil condenser. Normally I clean the glass slides and use the dry objective to do the measurement.

For the immersion oil condenser method, you can use the dry condenser first to align the oil condenser. This approach requires you to move the halogen lamp to the position of the objective. The space in the vertical dimension is quite limited. Make sure you will not damage the objective while moving things around. Again, clean off the immersion oil by using methanol and lens tissue after using it.





Figure 86 Condensers.

The other option is to use Silicon Nitride TEM grids. You do not need to use the grids unless you want to do it correlated with the STEM image. As I found, that in the opaque area of the TEM grids, the signal to noise ratio is very good!



Figure 87 Silicon Nitride support film, 15 nm.

It follows a very similar procedure as the photoluminescence & TCSPC measurement. First, start with the first grating, which will give you a nice image of the particles. You move the particles you want to see in the center region of the camera sensor, which is around 673 in terms of the x pixel number. Then you narrow down the slit all the way to the narrowest case where only 5-8 pixels are visible. Move to the third grating. Change the center wavelength to 650 nm (depending on the sample you measure). Use the regions of interest function to bin the y pixels of the particles together. 6-8 pixels to form a 6-8 by 1340 stripe of region. Set the exposure to 20 seconds and acquire the spectra.

The polarization measurement can be done by rotating the half-wave plate just before the polarizer. The polarizer is placed in front of the entrance of the spectrometer. The polarizer will be aligned in the vertical direction. The vertical direction should be the direction of the grating inside of the spectrometer. By rotating the half-wave plate by θ , the polarization selected by the polarizer will rotate 2θ . I still don't have a consistent way of knowing what the number on the half-wave plate corresponds to the polarization in the physical world. If you are doing measurement of the gold nanorods, it is easy to get the polarization by looking at the rods.

Filters:

The filters should be removed in the scattering measurements. A plate (empty filter holder) should be put in place to block the light from the surroundings. The long pass filters can also be removed and stored in the right place for later use. Don't touch these filters with fingers.

Static shock:

Discharge hands by touching on the optical table, before touching the slit knob, otherwise the shutter in the spectrometer can be damaged by the static shock.



Figure 88 Accessories of the microscope

Procedure for single particle optical/STEM correlated microscopy

In the correlated measurement, we first use the optical microscope in the lab to measure the optical properties of single particles (for example, photoluminescence for single QDs and scattering for plasmonic particles). Then we move the sample to the electron microscope.

 The sample preparation method for TEM grids was introduced in Chapter 2. It is always good to start with low concentration when depositing the sample. In this case, if you cannot see anything you can always reuse the grids and add more sample on it. In an example, I dilute the gold nanorod sample by a factor of 10. Then I put around 3.5 µl diluted sample on the TEM grids for 10 to 15 minutes. You might want to cover the grids so that the water does not evaporate too quickly. Before it dries out, I will use the tweezer to slide/surf the sample side on the clean water surface. Remember not to wet the other side!! The solution will be trapped in the other side. Then let the extra water dry for 10 to 20 minutes. A good concentration will be that around 20 to 40 particles in one window.

- 2. We made an adaptor to mount the TEM grids in the optical microscope. The sample side (smooth) should face down towards the objective. You should make sure the orientation of the TEM grids is roughly straight. This will make it easier to find other windows when you search for other particles. Remember, the opening area is very small compared to the whole area of the grids.
- 3. In the optical measurement, I used the LabVIEW program to record the location of the grids corners and particles. I used pixel (673,200) on the camera sensor as the reference. First, I moved a corner of the grids to the reference point, then I hit "save grids" button to record this position. Next, repeat this for most of the window corners. It might be a good idea to deliberately break one corner window by the tip of the tweezer. As a result, the symmetry is broken, and it helps you find the particles faster in STEM. Second, I measured the particle's optical properties, collected the data and recorded the particle position by clicking the "save particles" button.
- 4. The "saved" positions of the grids corners and particles will be used to recreate a map of the substrate, which is shown in Figure 45.

- 5. In the FEI microscope in the NanoImaging Facility, I used the STEM 2 mode to do the measurement. First, I loaded the TEM grids into the STEM sample holder. It is best to tilt the TEM grids holder to about 30 degree and let the gravity do the work. Then the TEM grids will slide into the position. In this step, I tried to make the orientation of the grids as straight as possible. As a result, the sample was only subject to 90-degree rotation as compared to the optical-microscope images. It is much easier to find the particles in this way.
- Around 30 minutes pumping is good enough to have some good images. The pressure is normally around 10⁻⁶ Torr. The energy of the electron was set at 30 keV. The spot size was 1.0.
- 7. It is easier to start the focusing process by imaging clusters of gold nanoparticles.
- 8. Take STEM images.



Figure 89 TEM grids holder and a TEM grids substrate. The smooth side of the TEM grids is facing down.

Procedure for COMSOL (FEM) calculation of scattering

spectra

Steps for simulating the scattering spectra of a gold nanoparticle in COMSOL:

1. Start COMSOL

- 2. Choose the wave-optics module and frequency domain for the study
- 3. Define the value for the parameters in the calculation, for example, dimension of the geometry, dielectric function parameters, and polarization angles
- 4. Define the geometry. The calculation domain needs to be larger than the size of the nanoparticle. For a 100-nm GNP, I will set the space as a sphere with 600 nm diameter. Then you can define a shell (100 nm thick) using the layer option. This shell will work as the perfectly matched layer, which absorbs the electromagnetic field.
- 5. The gold nanoparticle can be either defined or imported as a CAD file.
- You can partition and merge objects to improve the efficiency of the program.
 You can increase the resolution of the grids in some specific regions while decreasing the resolution of some other places.
- 7. You have at least three options regards the dielectric function of the material:
 - a. Use the built-in library, for example, Au (Rakic)
 - b. Use the interpolation function from the definition menu. A tabulated data of the dielectric function can be loaded into COMSOL. Then the data can be interpolated to use in the simulation. We downloaded data linked to journal articles for Ag and Au.^{54,55}
 - c. You can use the built-in model to define your material. This function can be found in "Electromagnetic waves, frequency domain/ Wave equation, electric/ electric displacement field". We used the Drude-Lorentz model to define the dielectric function of deformed gold nanoparticles under vibration.

- 8. For simple scattering spectra, you can use the scattered-field setup. In the frequency domain (except for the perfectly matched layer), select only the scattered field will be calculated. In the "Electromagnetic waves, frequency menu", you can define the background field. You can define the polarization of the field here.
- 9. Then in variable section, you can define the Poynting vector as *"ewfd.relPoavx*nx+ewfd.relPoavy*ny+ ewfd.relPoavz*nz"*. The surface integral of this Poynting vector will be the magnitude of the scattering from the nanoparticles. The surface integral can be defined on a surface surrounding the nanoparticle.
- 10. The mesh of the domain is very important, as it defines the quality of the result. You can always increase the resolution to have better results, but it will also significantly slow down the calculation. If possible, the simulation should be done in 2D. Several test runs with different grid resolutions can tell how the result depends on the resolution.
- 11. In the study, the frequency will be swept. You can sweep other parameters too in the parametric sweep setting.
- 12. The results can be plotted in 1D, 2D and 3D to visualize different quantities.

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Figure 90 An overview of the COMSOL interface.

In some cases, the scattered field setup will not be appropriate, for example, the calculation of the gap plasmon. In the case of a gap plasmon, the metal film will be very large and cannot be approximated by a uniform background field. In this case, we can run the simulation twice, once with the metal film only, then with the GNP. In the second run with the gold GNP, the background field is the result from the first run with the metal film only.

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