Photoluminescence of metallic plasmonic nanostructures

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**PHOTOLUMINESCENCE OF METALLIC
PLASMONIC NANOSTRUCTURES**

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**DIVISION OF PHYSICS & APPLIED PHYSICS
SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

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HU HAILONG

**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

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Summary

The applications of plasmonic nanostructures provide a promising way to achieve enhanced light-matter interaction and energy harvesting in future. In this thesis, the single-photon luminescence (PL) of noble metallic plasmonic nanostructures has been systematically investigated, demonstrating the plasmon effect in the energy conversion from non-equilibrium electrons to photons. The main emphasis of this thesis is laid on the physical mechanism of photoluminescence in metal nanomaterials and the exact role of plasmon in this process.

The photoluminescence spectra are collected by a micro-PL system from single isolated Au nanostructures fabricated by electron-beam lithography (EBL). It is well-known that EBL is able to produce plasmonic nanostructures with any arbitrary geometrical and dimensional nanostructures, promising the possibility of tunable plasmon resonance frequency within nanometer accuracy. Dark field scattering microscopy is used to obtain the plasmon resonance spectra of metal nanostructures. Strong shape-and size-dependent PL spectra are observed, showing very close correlation in peak position and spectral width with scattering spectra. These systematic results directly reveal that the PL peaks of individual Au nanostructures are indeed the consequence of radiative damping of plasmon resonance driven from optically excited electrons, instead of the direct recombination of *sp* electrons and *d* holes. The experimental results also show a universal blue shift in the PL peak positions with respect to the corresponding plasmon resonance peaks due to the inhomogeneous population distribution of non-equilibrium electrons available for the excitation of plasmon. More importantly, we have also observed the partial

polarization of the PL emission spectra where the PL peaks show stronger intensity along the same polarization direction of the incident laser. The simulated absorption and scattering spectra provide strong theoretical support for our conclusions. The detailed plasmon-modulated PL process is described *via* a simple physical mechanism model, also giving a rough prediction of PL spectra of plasmonic nanostructures.

The effect of plasmon coupling with single-photon luminescence is studied for the first time through two typical plasmonic nanostructures: isolated Au nanodisk dimers and single Ag nanowire-Al₂O₃-Au film. Strong luminescence spectra are determined by the radiative decay of coupled plasmon modes rather than intrinsic mode, for instance, longitudinal and transverse plasmon resonances in dimers, as well as the gap plasmonic nanocavity in nanowire-film system. It is found that tunable PL spectra could be achieved by adjusting the gap distance of nanodisk dimer or the diameter of Ag nanowire. The simulations of absorption and scattering spectra are conducted to confirm and understand our observations. These results provide more conclusive evidences about the origin of PL from plasmonic nanostructures and should also remove any doubts of the role of plasmons in PL.

The plasmon-enhanced photoluminescence of Au nanoparticles array prepared by nanosphere lithography are visualized by using an optically trapped polystyrene microsphere. This method without the involvement of any plasmon allows us to not only obtain the near-field intrinsic PL images but also compare the PL spectra at different positions with higher spatial resolution (~100 nm). Strong PL hot spots are observed from the gap center of each nanotriangle dimer just parallel to the laser polarization direction. Obvious polarization dependence of near-field PL images is

obtained due to the strong local electromagnetic field induced by plasmon resonance. This study provides the possibility to obtain near-field understanding about PL spectra and intensity distributions of plasmonic nanostructures.

All experimental results and analyses presented in this thesis could benefit not only the fundamental understanding about the plasmon-modulated dynamics of energetic electrons but also the exploration of plasmon-based photonic or hot-electron devices.

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Abbreviations

PL	Photoluminescence
EBL	Electron-beam lithography
NSL	Nanosphere lithography
ALD	Atomic layer deposition
FDTD	Finite-difference time-domain
SEM	Scanning electron microscopy
TEM	Tunneling electron microscopy
SPR	Surface plasmon resonance
DOS	Density of states

Publications

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10. **H. L. Hu**, C. X. Cong, Y. Ma, T. Yu, and Z. X. Shen, “Visualization of plasmon-enhanced

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Chapter 1 Introduction

Energy conversion between photons and energetic electrons is always one of important research topics. In the past two decades, it has been extensively demonstrated that surface plasmon resonance of noble metal nanostructures is able to drastically enhance the light-matter interactions. Such capabilities of metal nanostructures indeed refer to the extreme concentration of external light and the huge local electromagnetic field when their plasmon resonances are excited. Recently, the plasmon-mediated transformations of excited electrons are attracting numerous attentions due to the great potential applications in photodiodes, coherent plasmonic light source (cathode-luminescence) and high efficient chemical catalysts.

Single photoluminescence indeed reflects the energy transfer from nonequilibrium electrons to photons. I have systematically studied single-photon luminescence of individual plasmonic nanostructures using a micro-PL system. I utilize dark field scattering spectroscopy to characterize the correlated plasmon resonances of metal nanostructures. Electron-beam lithography provides a promising control for the plasmon resonance frequency *via* varying the shape, size and gap distance of gold nanostructure. I use atomic layer deposition to achieve insulator layer with a few nanometers thickness between Ag nanowire and Au film. I present the detailed analysis of PL spectra including peak position and peak width. The comparisons of photoluminescence, scattering spectra and SEM image for the same nanoparticle allow obtaining the direct evidences about the physical mechanism and

the exact role of plasmon. These investigations give deeper insight into the details of the PL process and should also remove any doubts of the role of plasmons in PL.

This whole thesis is organized as follows:

In Chapter 2, I will briefly introduce the fundamentals about optical response of noble metal *via* a frequency-dependent complex dielectric constant in Drude and Drude-Lorentz models. I will present the basic definition and features of two important surface plasmon resonances, namely, propagating and localized surface plasmon resonances. Then the size, shape and coupling effect in localized surface plasmon resonances will be mainly discussed. Additionally, the current status and open questions for single photoluminescence of noble metal nanostructures will also be introduced.

In Chapter 3, I will describe the details about sample fabrications, optical measurements and theoretical FDTD simulations.

In Chapter 4, I will present systematic PL results obtained from individual Au nanostructures fabricated by electron-beam lithography. By correlating the PL with scattering spectra, I will mainly discuss the underlying physical mechanism and the role of plasmon in this process based on the shape, size and polarization effect for PL.

In Chapter 5, I will mainly focus on the effect of plasmon coupling in single photoluminescence of Au nanodisk dimer with varied gap distance and single Ag nanowire-Al₂O₃-Au film. Our findings shown in this chapter provide very conclusive evidence about the exact origin of photoluminescence.

In Chapter 6, I will visualize the plasmon-enhanced photoluminescence of Au

nanoparticles array using an optically trapped polystyrene microsphere. The influence of excitation polarization on near-field PL image will be investigated.

In Chapter 7, I will give a brief summary about our understanding of single-photon luminescence in plasmonics nanostructures. I will also discuss some necessary investigation about photoluminescence in future.

Chapter 2

Theoretical Background of Surface Plasmon and Photoluminescence of Noble Metals

Optical properties of noble metals (Au, Ag and Cu) have been extensively applied dating back to the ancient Chinese states (770 BC). Two typical application examples are bronze mirrors and colorful windows manufacture in Middle Ages, as shown in Figure 2.1. The latter has been demonstrated as mixture of colloidal Au nanoparticles with different shapes and sizes using scanning electron microscopy (SEM). So far, those shape- and size-dependent optical behaviors have been comprehensively understood as the collective oscillation of free electrons in noble metal with the existence of external electromagnetic wave, which is also termed as plasmon resonance.^{1,2} In the past two decades, optical response of metal nanoparticles have become one of attractive research topics since plasmon resonance is able to extremely focus the incident light into sub-wavelength region and simultaneously induce strong, highly localized electromagnetic field around nanoparticle surface.³ Such properties have been widely utilized to enhance light-matter interaction, for example, surface enhanced spectroscopy (Raman/fluorescence/infrared)⁴, solar cell⁵ and SPASER⁶. And a new sub-discipline of optics is subsequently developed as plasmonics.

Figure 2.1: Colorful glasses window in Cathédrale Notre Dame de Paris taken in 2011 by author.

It has been demonstrated that the red color was created by colloidal Au nanoparticles with various shapes and sizes.

2.1 Optical properties of noble metals

2.1.1 Drude and Drude-Lorentz models

Theoretical understanding of optical properties of noble metals is not only fundamental interest but also the requirements for potential applications. It is well-known that the intriguing optical responses of metal for incident light are mainly determined by their free electrons. When an electromagnetic wave is illuminating metal, it could induce the relative displacement between free electrons and ion charges, then resulting in the charge collective oscillation due to the electrostatic restoring force, which is also known as plasmon resonance. This phenomenon was firstly described through a frequency-dependent complex dielectric constant (ε_m) by Paul Drude in 1900.⁷ In the Drude model, metal was treated as a simple mixture of ideal electron gas in conduction bands and positively-charged ions without the existence of the interaction between electrons. The complex dielectric function of metal was often expressed as $\varepsilon(\omega) = \varepsilon_{re} + i\varepsilon_{im}$,

$$\begin{aligned}\varepsilon(\omega) &= \varepsilon_{re} + i\varepsilon_{im} = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \\ &= \varepsilon_{\infty} - \frac{\omega_p^2}{(\omega^2 - \gamma^2)} + i \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)}\end{aligned}\quad (2.1)$$

$$\omega_p^2 = \frac{ne^2}{\epsilon_0 m} \quad (2.2)$$

Where ω is the frequency of incident light, γ is damping frequency of electrons, and ϵ_∞ shows the constant polarization contribution from positive metal ions. ω_p represents the bulk plasmon frequency of metal in free space (ϵ_0) in accordance with charge density n , electron charge e and effective electron mass m . Note that the bulk plasmon energy of Ag and Au are 8.55 and 9.60 eV respectively, locating in the ultraviolet (UV) regions.⁸

Figure 2.2: Real and imaginary parts of dielectric constant of gold (a) and silver (b) ranging from 300 to 1000 nm. The corresponding dielectric function obtained from the classical Drude and Drude-Lorentz models are plotted in the black and red curves. The electronic interband and intraband transitions of metal have been taken into account in Drude-Lorentz model. The experimental data from Johnson-Christy⁹ in green curve are in good quantitative agreement with Drude-Lorentz model, however, showing significant deviation from Drude model especially in the gray region ($\lambda \leq 600$ nm).

For Au and Ag, the calculated real and imaginary parts of dielectric constant from Drude model in the optical region are shown as the black curves in Figure 2.2a

and b , respectively. For comparison, the experimental data measured by Johnson and Christy in relevant region are also plotted in Figure 2.2. At long wavelength region ($\lambda \geq 600$ nm), it is remarkable that, for Au, theoretical prediction using the Drude model for both real and imaginary curves are very close to experimental ones. Note that the imaginary part plays a dominant role in the dielectric constant in this wavelength area. However, at short wavelength region ($\lambda \leq 600$ nm), there are crucial deviations between Drude model and experimental results, as shown in the gray regions in Figure 2. Indeed, these mismatches were the consequence of electronic interband transitions from d bands below Fermi level to sp conduction bands induced by the absorption of incident light, which were then amended in Drude-Lorentz model.

In a first approximation, the interband transition was assumed as a summation of Lorentz oscillators taking the bulk band structure in to account. Therefore, an additional term, $\varepsilon_{inter}(\omega)$ was added to the Drude formula (1), describing the contribution of interband transition to the dielectric constant.¹⁰

$$\varepsilon(\omega) = \varepsilon_{Drude}(\omega) + \varepsilon_{inter}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} + \left(-\frac{\Delta\varepsilon\Omega_p^2}{\Omega_p^2 - \omega^2 - i\Gamma\omega} \right) \quad (2.3)$$

Here, $\Delta\varepsilon$ represents the contribution of certain interband transition. Ω_p and Γ are the Lorentz oscillation and decay frequencies for the bound electrons. Obviously, the Drude-Lorentz model gives better match with experimental data in the whole optical region. Note that the Drude part was modified accordingly with this consideration of interband transition.

2.2 Surface plasmon resonance in metal nanostructures

The promising applications of metal nanostructures, for instance, in colorful printing¹¹, single molecule detection¹² and subwavelength focusing¹³, are indeed the consequences of another important plasmon behavior of these structures in visible-infrared regions, which is well-known as surface plasmon resonance (SPR). Different from bulk plasmon resonance, this resonance often occurs either along the interface of metal film-dielectric or metal nanoparticles. Note that there are some

basic differences between them. I will simply introduce some characteristics of metal film plasmon resonance for comparison and then mainly focus on the case of localized one.

2.2.1 Propagating Surface plasmon resonance in planar metal film

Figure 2.3: Schematic illustrations of two typical plasmon resonances: (a) surface plasmon polariton of planar metal film and (b) localized surface plasmon of metal nanoparticles.

For planar metal film, as shown in Figure 2.3a, the plasmon resonance generates alternating positive-negative charges distribution along the x-directional interface, leading to the propagation of surface plasmon resonance, thus called as propagating surface plasmon polaritons (SPP).¹⁴ So far, such propagation has been demonstrated to be over centimeter length scales from Ag stripe, indicating the great capability as photonic device.¹⁵ The correlated oscillation frequency follows the SPP dispersion between momentum and energy, which could be obtained from Maxwell's electromagnetic equations with suitable boundary conditions. This SPP wave-vector, κ_{spp} , is often expressed as below. The details about it could refer to some good literature reviews.^{16, 17}

$$k_{spp} = k_0 \sqrt{\frac{\epsilon_s \epsilon_m}{\epsilon_s + \epsilon_m}} \quad (2.4)$$

Where κ_0 is the wave-vector of incident light in free space, ϵ_s and ϵ_m are the dielectric function of surrounding dielectric and metal, respectively. Note that the plasmon frequency depends highly on the refractive index of surrounding. So far, a

class of high sensitive index-SPR sensors, especially for bio-molecule detections, has been intensively developed from this strong environmental dependence of plasmon frequency.

2.2.2 Localized Surface plasmon resonance in metal nanoparticle

Different from propagating SPP, the electron oscillations in metal nanostructures with the size much smaller than the incident wavelength are mainly localized within structures, which is also termed as localized SPR or particle plasmon as presented in Figure 2.3.b.¹⁸ Note that, in the whole thesis, plasmon means localized SP instead of SPP if there is no particular explanation. The excitation of particle plasmon resonance in metal nanoparticles always leads to the drastic enhancement in absorption and scattering efficiencies for photons with the resonant energy.^{2, 19} Such localization results in extreme concentration of light and an enhanced electric field around nanostructures, subsequently affecting the interaction between incident light and other matter close to the surface of nanostructures. The first analytical electrodynamics solution to Maxwell's equations for metal nanospheres was described using by Gustav Mie in 1908.²⁰ Note that, in practice, Mie theory could be appropriate for only nanospheres with arbitrary sizes before the extension by Richard Gans in 1912.

The optical response of metal nanoparticles could be generally described using an important parameter, extinction cross section (σ_{ext}), defining as the total summation of absorption (σ_{abs}) and scattering (σ_{sca}) cross section,

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca} \quad (2.5)$$

Note that absorption and scattering processes are related to the photons converted into thermal energy and deviated from the original direction, respectively, as shown in Figure 2.4. Normally, the absorption and scattering cross sections is proportional to the geometrical cross section A .

Figure 2.4: Schematic diagrams of absorption (a) and scattering (b) cross section of sphere. Q_{abs}

and Q_{sca} are the dimensionless absorption and scattering coefficient, respectively.

In Mie theory, the extinction coefficient is used to describe the total absorption and scattering of incident light induced by electric and magnetic dipole or multipole oscillations. For symmetric nanosphere, the scattering and extinction cross section could be generally expressed,

$$\sigma_{sca} = \frac{2\pi R^2}{x^2} \sum_{n=1}^{\infty} (2n+1) [|a_n|^2 + |b_n|^2] \quad (2.6)$$

$$\sigma_{ext} = \frac{2\pi R^2}{x^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}[a_n + b_n] \quad (2.7)$$

Where $x = 2\pi R n_0 / \lambda$ is defined as particle size parameter, n_0 is the refractive index of the surrounding, R is the radius of the nanoparticle. a_n and b_n are the Mie coefficient, representing the electric and magnetic amplitude for a given n oscillation mode. These two parameters often run as a function of the relative index between metal nanosphere and surrounding in the general expression as (2.7) and (2.8),

$$a_n = \frac{\psi'_n(mx)\psi_n(x) - m\psi_n(mx)\psi'_n(x)}{\psi'_n(mx)\xi_n(x) - m\psi_n(mx)\xi'_n(x)} \quad (2.8)$$

$$b_n = \frac{\psi_n(mx)\psi'_n(x) - m\psi_n(x)\psi'_n(mx)}{\psi_n(mx)\xi'_n(x) - m\xi_n(x)\psi'_n(mx)} \quad (2.9)$$

Here, $m = n_m/n_o$ is the relative refractive index between metal nanospheres and environment. $\psi_n(x)$ and $\xi_n(x)$ are the Riccati-Bessel functions.

For metal nanosphere with size parameter $x \ll 1$ or the diameter below 40 nm, the Mie theory could be simplified using the first order approximation ($n = 1$),

ignoring the influences from quadrupolar, octupolar and higher-order multipolar plasmonic modes. Then Mie scattering of metal nanosphere becomes equivalent to the quasi-static plasmon resonance Rayleigh scattering. The absorption and scattering cross section of single sphere given by Bohren and Huffman could be described using its polarizability α .⁸

$$\sigma_{abs} = k\text{Im}(\alpha) = 3kV \frac{3\varepsilon_r''}{((\varepsilon_r' + 2)^2 + \varepsilon_r''^2)} \quad (2.10)$$

$$\sigma_{sca} = \frac{k^4 |\alpha|^2}{6\pi} = \frac{k^4}{6\pi} (3V)^2 \frac{(\varepsilon_r' - 1)^2 + \varepsilon_r''^2}{((\varepsilon_r' + 2)^2 + \varepsilon_r''^2)} \quad (2.11)$$

with $= 3V\varepsilon_0 \frac{\varepsilon_r - 1}{\varepsilon_r + 2}$, the relative index between metal nanosphere and surrounding

$\varepsilon_r = \varepsilon_r' + i\varepsilon_r'' = \varepsilon_m/\varepsilon_s$, and the particle volume V .

When $\varepsilon_r' + 2 = 0$, namely, $\text{Re}(\varepsilon_m) = -2\varepsilon_s$, the particle plasmon resonance in metal nanosphere is excited, roughly estimating maximum absorption and scattering cross section.² The resonant condition also suggests that the plasmon frequency is highly dependent upon the dielectric constant of surrounding, as demonstrated by metal nanoparticle sensors.²¹

Moreover, in experiments, this plasmon resonance frequency shows obvious red-shift with the increase of nanosphere diameter. In Mie theory, this size dependent optical signature is rationalized because the damping frequency (γ) of electrons in dielectric constant of metal nanosphere is indeed a function of the particle radius (R),²²

$$\gamma(R) = \gamma_b + \frac{Av_F}{R} \quad (2.12)$$

where γ_b and v_F are the bulk damping constant and Fermi velocity, respectively. A is theory-dependent parameter relying upon the electron scattering.

When metal nanospheres have size parameter x larger than 1, the quasi-static approximation would be no longer accurate. The contribution from multipolar plasmon mode and electromagnetic retardation should be taken into account.¹⁰

With the advanced chemical synthesis and physical fabrication approaches, metal nanoparticles with various shapes,^{23, 24} for example, rod, triangle, cube, could be

easily achieved. It is found that the particle shape plays a more pronounced role in plasmon resonance frequency. However, as mentioned above, the Mie theory could not be suitable for non-spherical nanoparticles. Then the Mie theory was extended into the case of oblate and prolate spheroidal particles by Richard Gans in 1912, which is called as Gans theory or Gans-Mie theory.²⁵

For an small prolate spheroid with three principal axes a , b and c ($a > b = c$), the polarizability α could be expressed as follows,

$$\alpha_i = \frac{4}{3}\pi abc \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_s + (\varepsilon_m - \varepsilon_s)P_i} \quad (2.13)$$

where P_i is defined as the geometrical polarization factor along one axis,

$$P_a = \frac{1 - e^2}{e^2} \left[\frac{1}{2e} \ln \left(\frac{1 + e}{1 - e} \right) - 1 \right], \quad e = \sqrt{1 - \frac{b^2}{a^2}} \quad (2.14)$$

$$P_b = P_c = \frac{1 - P_a}{2} \quad (2.15)$$

with the total polarizability factors $P_a + P_b + P_c = 1$ and the aspect ratio a/b . Consequently, the free electrons in metal nanospheroid independently oscillate along the long and short axis, resulting in the formation of two plasmon resonance frequencies, longitudinal and transverse modes, as presented by single Au nanorod in Figure 2.5. In experiment, the tunable longitudinal plasmon frequency could be achieved through varying the aspect ratio of nanospheroid.

Figure 2.5: Dark field scattering spectrum of single Au nanorod with the aspect ratio of 2, showing two pronounced plasmon resonant peaks. The peak at long wavelength (580 nm) is attributed to the collective oscillation along the long axis, thus named as longitudinal mode. And the transverse mode due to the oscillation along short axis is correlated to the peak at short wavelength (560 nm). The longitudinal mode is highly dependent upon the aspect ratio, show significant shift towards longer wavelength for larger ratio.

Two attractive optical characteristics of metal nanostructures due to the collective oscillation at plasmon frequency are extreme concentration of incident light and strong local electromagnetic field.³ Moreover, the plasmon resonance frequency could be tunable from the visible to infrared (IR) region by changing shape, size or dielectric surrounding.²¹ Such properties provides promising enhancement on the light-matter interaction, for instance, Raman/IR/photoluminescence signals,⁴ light absorption efficiency in solar cell⁵ and nonlinear second-harmonic generation (SHG)²⁶. In order to better understand the magnitude of extinction cross section, I compare the extinction cross section of metal nanostructures with other three types of optical species,²⁷ for instance, atoms or ions, organic dyes, and semiconductor quantum dots, as depicted in Figure 2.6. Obviously, plasmon nanostructures have the largest extinction cross section in these sub-wavelength optical objects. And the fact that the ratio between extinction and geometrical areas of plasmon nanostructures is larger than one also reflects the capability to absorb or scatter incident light.

Figure 2.6: Optical extinction cross section (a) and coefficient (b) of four types of nanoscale optical species.

2.3 Plasmon coupling

As discussed above, the plasmon resonance of metal nanoparticles is very sensitive to the local chemical environment. What will occur if two metal nanoparticles are very close? It has been widely demonstrated that the plasmon coupling between nanoparticles shows significant red or blue shift in resonance frequency with respect to the case of individual nanoparticle, also resulting in the pronounced color change.²⁸ And the coupling generates enormous local electric field between nanoparticles, contributing to the formation of hot spots with $10^{14} \sim 10^{15}$ enhancement factor for surface-enhanced Raman scattering (SERS).²⁹ Importantly, the plasmon coupling has produced several striking optical phenomena, such as, electromagnetic induced transparency (EIT),^{30, 31} Fano resonance,³² and optical chirality.³³ In the section, I will focus on the theoretical understanding of plasmon coupling between nanoparticles.

The coupling could be understood by either the simple harmonic oscillator model^{10, 28} or analytical plasmon hybridization proposed by P. Nordlander and N. J. Halas.³⁴⁻³⁶ The latter one provides a quantitative picture of the plasmon resonances in even very complex nanostructures. Taking nanoparticles dimer and nanoparticle-film

as two typical examples is to briefly introduce the basic concepts of these two approaches.

In harmonic oscillator model, the electron oscillation is the consequence of repulsive force, towards the direction of positive ions. The plasmon coupling could give rise to anisotropic optical responses. For nanoparticle dimer, when external electromagnetic field is parallel to the long axis of dimer, as shown in Figure 2.7a, the local field induced by the top particle produces additional attractive electrostatic force on the bottom particle, resulting in the decrease of repulsive force and red shift in plasmon resonance frequency. In contrast, in the case of perpendicular excitation in Figure 2.7b, the plasmon frequency of dimer shifts to short wavelength region with respect to the case of single nanoparticle. When nanoparticles are placed on metal film with small gap, an image dipole in metal film is induced by the excited plasmon resonance of metal nanoparticles, as depicted in Figure 2.7c and d. Analogously, under both normal (c) and parallel (d) conditions, the interaction between real and image dipoles decrease the plasmon resonant frequency.

Figure 2.7: Schematic pictures of plasmon coupling in nanoparticle dimer (a-b) and nanoparticle-film (c-d). The interaction could be understood through an additional electrostatic attractive or repulsive force between them, leading to red or blue shift in plasmon frequency with the respect to single nanoparticle.

Borrowing the hybridization concept of Hückel molecular orbital method,³⁷ P. Nordlander and N. J. Halas developed analogous plasmon hybridization (PH) to

provide straightforward description of the plasmon interaction between nanoparticles. In PH model, noble metals and their nanostructures are assumed as incompressible and irrotational fluidic electrons restricted in uniform positive background. From Figure 2.8, we can see that, after hybridization, the primitive identical plasmon resonance of two nanospheres (ω_{sp}) convert into a bonding/bright mode ($|\omega_{-}\rangle$) with lower energy and an anti-bonding/dark one ($|\omega_{+}\rangle$) with higher energy. The bonding mode which is corresponding to the case in Figure 2.7a could be optically excited. Note that the primitive plasmon frequency ω_{sp} is mainly determined by the particle shape. Comparing with the classical model, the PH approach has own advantage in understanding the coupling of dipole-dipole and dipole-multipole plasmon modes even in complex nanostructures.

Figure 2.8: Schematic view of plasmon hybridization between two close nanospheres. The principle of this model is analogous to the hybridization of Hückel molecular orbital method (HMO). The plasmon coupling forms a binding resonance mode with lower energy and an anti-bonding mode with higher energy.

2.4 Dynamics of particle plasmon resonance

The fundamental dynamics of plasmon resonance in metal nanoparticles has been of great interest for the applications enhancing light-matter interactions. Oscillation amplitude and lifetime of plasmon resonance are two useful parameters of dynamic property. Taking SERS as a typical example, a plasmon resonance with

larger oscillation amplitude and longer lifetime often leads to stronger Raman enhancement.^{19, 38} Here, I briefly introduce the damping mechanism and process in time scale of plasmon resonance metal nanostructures.

After the excitation of conduction electrons, the coherence of plasmon oscillation could be perturbed via the collision with electrons, phonons, defects and impurities. Normally, the plasmon decay could occur through two main channels, radiative and nonradiative damping.³⁸ As presented in Figure 2.9a, for certain plasmon resonance (ω_{sp}), the radiative decay always leads to the emission of photons with the same frequency (ω_{sp}) as plasmon, which is indeed observed as scattered light. On the other way, the excited electrons could nonradiatively lose their energies through exciting unexcited electrons in *sp* and *d* bands below Fermi level via intraband and interband transitions, respectively. These two transitions are corresponding to photon absorption. When the plasmon resonance has lower energy than the transition in noble metals (Ag: 4eV, Au: 2.4 eV), as demonstrated by the longitudinal mode of Au nanorods,³⁸ the interband transition could be drastically suppressed and the plasmon shows longer lifetime and higher quality factor.

The lifetime of coherent electrons oscillation in metal nanostructures is in a very short time, within the order of a few femtoseconds (fs) due to strong radiative and nonradiative damping. The total decay time T_2 is often described as,³⁹

$$T_2^{-1} = \frac{T_1^{-1}}{2} + T^{*-1} \quad (2.16)$$

T^* and T_1 represent the time constant of pure dephasing and inelastic decay, respectively. A rough decay picture in time scale in Figure 2.9b has been obtained from systematical analysis of femtosecond transient absorption spectra and the full width at half maximum (FWHM) in extinction spectra of metal nanoparticles.⁴⁰⁻⁴²

Firstly, the plasmon resonance can be quickly destroyed by pure dephasing within 10 fs, forming a non-equilibrium electron distribution. Then the electron-electron scatterings would generate hot electrons at 10^2 fs, which now attracts increasing attention from in various areas due to the great potential application as visible/IR optical photodiodes and chemical catalysts. Finally, electron-phonon scattering

occurring at 10^3 fs gives rise to the phonon vibrations, converting into thermal energy.

Figure 2.9: Decay dynamics of optical excited plasmon resonance of metal nanoparticles. (a) Radiative and nonradiative dampings are two important decay ways of plasmon resonance. The former eventually emits a photon with the same plasmon frequency. And the latter gives rise to interband or intraband transitions. (b) The decay process of plasmon resonance occurs at different time through radiative and nonradiative decays.

2.5 Single-photon luminescence of noble metals and nanostructures

2.5.1 photoluminescence of bulk noble metals

The optical applications of plasmonic metal nanostructures are mainly determined, in principle, by the intrinsic optical response of free electrons and its radiative/nonradiative coupling strength with other active matters like probing molecules and semiconductor. It is well-known that single-photon luminescence (PL) has been early observed from semiconductor, representing the inelastic combination between electrons in conduction band and holes in valence band.⁴³ Indeed, PL also reveals the population distribution of these non-equilibrium electrons in energy scale after a variety of thermalization processes.⁴² However, less attention has been paid on the case of metal.

A visible and broad photoluminescence was firstly reported from noble metal (Au and Cu) films in 1969 by A. Mooradian⁴⁴, as Figure 2.10a. In light of PL

mechanism of semiconductor, as shown in Figure 2.10b, this single photon luminescence could be demonstrated by a three-step process: (1) interband transition of electrons from d-bands below the Fermi level to sp-conduction bands above the Fermi level *via* photon absorption; (2) formation of electron-hole pair around Fermi level through thermal relaxation of these optical excited electrons and holes by electron-electron and electron-phonon scattering; (3) radiative recombination of these electron-hole pairs. Therefore, the photoluminescence of bulk noble metal indeed reflects the population distribution of optically excited electrons after several thermalization events. And the photoluminescence peak illustrated in Figure 2.10a was attributed to the interband transition due to the large optical density of states.⁴⁵ However, the probability of such recombination is very low owing to the dominant nonradiative relaxation processes. For instance, the one-photon PL efficiency of bulk gold is as low as 10^{-10} .

In 1986 G. T. Boyd *et al.* provided quantitative description about those three processes above to understand and calculate the photoluminescence.⁴⁶ A general differential expression for photoluminescence from metal was given as follows,

$$I_{PL}(\omega_2)dz = I(\omega_1, z) * Y_{1,abs} * Y_R * Y_{PL}dz \quad (2.17)$$

here ω_1 and ω_2 represent the frequency of incident light and photoluminescence, respectively. $I(\omega_1, z)$ is the power intensity of incident light at z depth from surface. $Y_{1,abs}$ is defined as the photon absorption efficiency for ω_1 . Y_R reflects the relaxation probability of the excited electrons and holes into electron-hole pairs. Y_{PL} is the emission probability of electron-hole at ω_2 through radiative recombination.

By this simple expression (2.17), band structure and Fermi Golden rule, the one photon luminescence of bulk metal could be roughly calculated, which benefited to comprehensively understanding the underlying physical mechanism. At the same time, they did the first comparison about the photoluminescence intensities obtained from smooth and rough Ag, Au and Cu film, finding that strong emission was produced by rough sample. Then this finding was explained as the consequence of local electric field created between non-touching hemispheroids in rough film, which is similar to the observation of SERS enhancement from rough metal electrodes⁴⁷ and second

harmonic generation⁴⁸.

Figure 2.10: (a) PL spectra of bulk Au film under the excitation of 457 and 532 nm laser, showing a prominent peak around 512 nm (2.4 eV). This PL was explained as the radiation combination of electrons in sp-conduction bands and holes in d-bands, as shown in (b).⁴⁴ Note that the peak around 560 nm in black curve is due to the cut-off of 532 nm long pass edge filter.

2.5.2 Photoluminescence of noble metal nanostructures

In the past two-decade, noble metal nanoparticles with arbitrary shape and size have been achieved by either bottom-up (chemical) or top-down (physical) methods.²⁴ Plasmon resonances of metal nanoparticles have the ability to dramatically enhance the local electromagnetic field and provide high optical density states for transition or relaxation, demonstrated by single molecular fluorescence detection⁴⁹ and lasing SPASER¹⁶. At the same time, the photoluminescence of metal nanoparticles has shown its importance for comprehensive understanding of plasmonics. It was inspiring to first observe a million enhancement of fluorescence ($10^{-4} \sim 10^{-3}$) from an ensemble of Au nanorods by Mohamed et al.⁵⁰ Moreover, it was found that the fluorescence peak displayed obvious blue shift with respect to the absorption peak, but showing similar red shift to absorption with increasing the aspect ratio of nanorods. Such property actually reflected the intrinsic relationship between fluorescence and plasmon resonance in nanoparticles. However, this phenomenon was explained as the result of local electric field according to Boyd's model.

Figure 2.11: Two representative models for plasmon luminescence of noble metal nanoparticles proposed by E. Dulkeith et al.⁵¹ (a) and A. Tcherniak et al.⁵² (b), respectively.

In 2004, E. Dulkeith et al. systematically studied the photoluminescence of colloidal Au nanospheres with the diameters ranging from 2 to 60 nm, and surprisingly observed obvious red-shifted luminescence peak with the increase of diameter.⁵¹ Moreover, it was also found the spectral overlapping in peak position between photoluminescence and extinction spectrum. According to such observations, they described the luminescence as the radiative emission of particle plasmon formed by sp electrons and excited d band holes, rather than the direct recombination of sp electrons and d band holes, which is different from the semiconductor-like PL mechanism. In order to understand those phenomena, they proposed the first plasmon-induced PL mechanism based on thermalized optical excited electrons and holes form particle plasmon, resulting in plasmon emission through radiation decay, as shown in Figure 2.11a.

Very recently, the relationship between plasmon luminescence and plasmon resonance has been further demonstrated on single Au nanorod by A. Tcherniak and his coworkers.⁵² The significance of PL study on single nanoparticle could indeed avoid the influence from the unknown particle shapes, size inhomogeneity and particles aggregation. They found that Au nanorods excited by 514 nm laser showed two luminescence peaks and only one peak excited by 633 nm. These two peaks were identified from the radiative damping of longitudinal and transverse plasmon resonances by correlating PL with the scattering spectrum. The luminescence peak

also showed the almost identical red shift as scattering peak when the sample was placed into water. Moreover, they noticed that the plasmon luminescence exhibited the same dipolar emission spatial distribution as scattering.

Another central aspect of plasmon luminescence was done to investigate the influence of excitation polarization on longitudinal and transverse luminescence intensities. Interestingly, Au nanorod showed different optical response with different excitation polarizations of 514 and 633 nm lasers. For 514 nm excitation, no matter whether the laser polarization was set parallel to the long or short axis of nanorod, the polarized luminescence exhibited identical intensity along long axis, indicating the independence of excitation polarization. And the luminescence from transverse plasmon resonance showed similar independence with longitudinal one. When excited by 633 nm laser, however, Au nanorod emitted as a dipolar oscillator, producing the strongest plasmon luminescence from longitudinal plasmon mode under parallel excitation condition.

A simple physical model was proposed to explain the plasmon luminescence of Au nanorods, as presented in Figure 2.11 b. The laser with the wavelength of 514 nm could excite the interband transitions ($d \rightarrow sp$) and transverse plasmon resonance simultaneously. The complete depolarization of plasmon luminescence was attributed to a quick transformation between excited electrons and longitudinal/transverse plasmon resonances. On the other hand, the interband transition in Au nanorod could not occur under the low energy excitation by 633 nm light, leading to a dipolar emission for longitudinal plasmon resonance.

2.6 Open questions

The study of single photoluminescence indeed benefits to comprehensively understand the pathways of electron energy relaxation in plasmonic nanostructures. The optical applications of plasmonic metal nanostructures are mainly determined, in principle, by the intrinsic optical response of free electrons and its radiative/nonradiative coupling strength with other active matters like probing molecules and semiconductor. To comprehensively understand the fundamental

dynamic of optically excited electrons, the investigation of single photoluminescence of plasmonic nanostructures is thoroughly central to understand two important aspects: i) the exact underlying physical mechanism and ii) the role of plasmon resonance.

For bulk noble metals, Mooradian and Body have given explicit explanations and quantitative description about the origin and spectral features of photoluminescence from smooth and rough metal film. And the origin of photoluminescence was accounted for the electronic interband transition. However, the mechanism for bulk metals had been intensively argued when applying to describe the million-fold enhanced photoluminescence observed from plasmon nanostructures in term of stronger Coulomb scatterings. More and more evidences have supported the new mechanism that PL of plasmonic nanostructures could be induced by the radiative decay of plasmon resonance excited from optically excited electrons. However, there is still under debate concerning the following two aspects: i) the exact underlying physical mechanism and ii) the role of plasmon resonance.

In experiment, taking the shape and size dependent plasmon resonance into account, a possible approach to concentrate those two problems is to investigate the PL of individual plasmonic nanostructure. However, all current PL measurements have been performed only on single crystalline metal nanostructures prepared by chemical synthesis. In this case, it is not easy to carry on a systematic PL study because of the complexity and difficulty to obtain the uniform shape and size by chemical synthesis. Is it possible to investigate the photoluminescence from the polycrystalline nanostructure fabricated by physical techniques? A systematic PL measurement in Chapter 4 has been done on a series of Au nanostructures like disk, rod and triangle fabricated by electron beam lithography, providing solid evidences for the PL mechanism.

Another open question regarding photoluminescence is the response of plasmonic nanostructures with different excitation polarizations. According to current literature results, PL emission has been observed insensitive to excitation polarization from colloidal Au nanospheres or single Au nanorod. However, the former suffered the nanoparticle's aggregation due to laser tweezers and inhomogeneous size

distribution in solutions. The latter shows anisotropic photon absorption and scattering along the long and short axis. Individual metal nanodisk with symmetric geometry is the best choice to solve this question, which will be discussed in Chapter 4.

An important feature of optical response is plasmon coupling in metal nanostructures. The influence of coupling has been found on two photon luminescence of coupled Au nanostructure. However, to be our best knowledge, there is no such work focusing on from how the plasmon coupling affects single photon luminescence. The PL results of Au nanodisk dimer with controllable gap distance provide the first look into the effect of coupling, as described in Chapter 5. Another typical investigation was concentrated on the photoluminescence due to the plasmonic gap nanocavity formed between single Ag nanowire and continuous Au film in Chapter 5.

The PL intensity distribution is also important to obtain a comprehensive understanding of this physical process. However, the conventional PL setup is unable to well resolve the nanostructure due to the far field diffraction limit. Near field measurements indeed require a technique that has no coupling with nanostructure. In chapter 6, I will provide a simple and appropriate near field approach to visualize plasmon-enhanced photoluminescence through optically trapping dielectric microsphere.

2.7 References

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Chapter 3

Sample fabrication, optical measurement and numerical simulation

In this chapter, the details about sample preparation, related optical measurement and numerical simulation will be mainly discussed. The experimental procedures in this thesis are shown in Figure 3.1. The photoluminescence and scattering spectra of individual Au/Ag nanostructures are mainly studied. Numerical simulations using finite-difference time-domain (FDTD) are carried out to confirm and understand the experimental results.

Figure 3.1: Schematics illustrating the experimental procedures in this thesis. The scattering and photoluminescence from plasmonic nanostructures fabricated by different methods were measured firstly and the scattering spectra were theoretically simulated by FDTD.

3.1 Fabrication of plasmonic nanostructures

Single-photon luminescence and scattering spectra of individual Au nanostructures, single Ag nanowire-Al₂O₃-Au film, and Au nanoparticles array were mainly investigated in this thesis. In order to study the photoluminescence and scattering of single nanostructure, we fabricated samples according to the following two criteria: 1) isolation from surrounding nanoparticles; 2) easy localization for

further measurements like scanning electron microscopy (SEM). Thus, we utilized electron-beam lithography (EBL) to precisely design their shape, size of single Au nanoparticle, and gap distance in its dimer. Large-scale Ag nanowires with various aspect ratios were synthesized by a chemical method, which were then spin-coated on Au film with very thin Al_2O_3 insulator above. And Au nanoparticles array were fabricated by nanosphere lithography (NSL). The details about the dimension for these three plasmonic nanostructures will be described in each chapter

3.1.1 Individual Au nanoparticles by EBL

To comprehensively investigate the plasmonic properties of single metallic nanostructures in the visible optical region (400-750 nm), it often requires the structure dimension within 100 nm, suggesting that the fabrication method is able to create the structure with precisely controllable shape and dimension. Electron beam lithography, as one of important top-down approach, has been widely used to generate nanoscale metallic structures even with sub-10 nm gaps.^{1, 2} Hence, in this thesis, individual Au nanoparticles (disk, rod, triangle and their dimers) with different size were fabricated on SiO_2/Si substrate by EBL using positive resist. Registration marks were also built to easily excite and collect the scattering and photoluminescence of single nanoparticle. The details of EBL processes, as shown in Figure 3.2, are described in the following step by step,

- 1) **Exposure.** Poly (methyl methacrylate) (PMMA) purchased from MicroChem Corp. (950K molecular weight, 1.67% in anisole) was chosen as positive resist,

which was spin-coated at 3 k rpm to be ~ 80 nm on SiO_2/Si substrates. The thickness of SiO_2 was 100 nm. The selection of silicon as the substrates as doing so avoids charging effects during the EBL process, while 100 nm SiO_2 was used as a spacer layer to reduce plasmon damping caused by the silicon substrate. Then the coated samples were baked on a hot plate at 180°C for 90 s. EBL was performed on an Elionix ELS-7000 system with an accelerating voltage of 100 kV and a beam current of 50 pA. Optimized dose was used to ensure the structures we designed for the optical studies of plasmonic nanostructures.

- 2) **Development.** After being exposed, the samples were developed with MIBK: IPA (1: 3) mixture at low temperature (-15°C) for 30 s and then were directly dried by a steady stream of nitrogen gas. Low-temperature development of PMMA provides higher contrast and pattern resolution.
- 3) **Gold deposition.** Metal deposition was performed using an electron-beam evaporator (Explorer Coating System, Denton Vacuum). A 30 nm Au layer was deposited with 1 nm Cr adhesion layer. The working pressure during the evaporation was $<5 \times 10^{-6}$ Torr. The temperature of the sample chamber was kept at 20°C during the entire evaporation process, with the sample holder rotating at a rate of 50 rpm to ensure the uniformity of deposition.
- 4) **Lift-off process.** The residual PMMA resist was ultimately lift off within N-Methylpyrrolidone (NMP) solvent at a relative high temperature of 70°C .

Figure 3.2: Four processes of Au nanoparticles fabrication by EBL, (1) exposure by electron beam; (2) development; (3) Au deposition; (4) lift-off. Note that PMMA was chosen as positive resist.

After these four processes, we obtained identical individual nanoparticle array with 2 μm spacing distance, as displayed in Figure 3.3, which is also related to chapter 4. From the dark field optical image, all nanostructures are marked.

Figure 3.3: Typical dark-field and SEM images of nanostructure arrays. (a) Dark-field optical microscope image of bowtie nanoantennas array. With marks, any individual isolated particle can be addressed for accurate scattering and photoluminescence measurements. (b) A SEM image of a 5 $\times$ 5 bowtie antennas array with high-resolution SEM image of a bowtie nanoantenna. (c) and (d) are the SEM images of nanorod and disk arrays attached with high magnification images of single and dimer structures. The SEM images were taken by an Elionix ESM-9000 system with an accelerating voltage of 10 keV.

3.1.2 Single Ag nanowire-Al₂O₃-Au film

Currently, plasmon coupling between metal nanoparticle and film, namely, gap plasmonic cavity, has been become one of great concern because of low non-radiative rate³ and huge local field enhancement⁴. In chapter 5, we chose single Ag nanowire-Al₂O₃-Au film as typical example to systematically investigate scattering and photoluminescence from the gap plasmonic nanocavity. The sample preparation procedure is shown in Figure 3.4 and the details are described in the following. 50 nm thick Au film was physically deposited on pure Si wafer by electron beam evaporation, then being coated with thin Al₂O₃ insulator by atomic layer deposition (ALD). Chemical synthesized Ag nanowires were finally dispersed on Al₂O₃-coated Au film using spin coating. The real cross section of Ag/Al₂O₃/Au structure is confirmed by transmission electron microscopy (TEM).

Figure 3.4: Schematic preparation process of monodispersed Ag nanowire-Al₂O₃-Au film by spin coating.

3.1.2.1 Chemical synthesized silver nanowires

Silver nanowires with various aspect ratios were chemically synthesized according to previous literature report.⁵ The detailed procedure of synthesis was described as following. 5 mL of ethylene glycol was heated under magnetic

stirring for 1 h at 151°C. Then, 40 μL of CuCl_2 (4 mM) was injected into the solution, which was further heated for 15 min. Then, 1.5 mL of PVP (147 mM) and 1.5 mL of AgNO_3 (94 mM) were added to the solution simultaneously. Ag nanowires solution was washed with purified water and ethanol and finally stored in ethanol for spin coating. The diameter and length of each Ag nanowire was obtained by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), shown in Figure 3.5.

Figure 3.5: Typical SEM image of silver nanowires with various diameters and lengths.

3.1.2.2 Al_2O_3 insulator layer coated by ALD

According to literature reports,^{6,7} gap size of particle-film has great influence on the plasmon coupling. How to obtain gap size within a few nanometers is still a big challenge and open issues. It is well-known that ALD is one of important methods that could allow us to precisely control the thickness of insulator within the atomic accuracy.⁸ Hence, in this case, Ag nanowire is isolated from continuous Au film by thin Al_2O_3 film coated by ALD. The detailed experimental process and condition are list as below. The deposition of Al_2O_3 was carried on a Beneq system (TFS 200) under 200 degree using trimethylaluminum [$\text{Al}(\text{CH}_3)_3$] and water as precursors. Nitrogen gas with high purity was the process gas in this coating. The deposition was done under the reaction chamber with the pressure of 1.0 mbar and a steady N_2 steam at 200 SCCM (cubic centimeter per minute). Each ALD cycle included a precursor pulse

(250 milli-seconds) and a subsequent purging (1 second) with N₂. The final film thickness was controlled by the numbers of the ALD cycles. The growth rate per cycle of Al₂O₃ is about 0.13 nm.

3.1.3 Au nanoparticles array by NSL

Nanosphere lithography developed from the self-assembly of nanospheres has been widely used to fabricate periodic nanoparticles array.⁹ In this experiment, we followed the technique reported by Rybczynski *et al.*,¹⁰ self-assembling a monolayer of highly ordered nanospheres on water surface and then transferring to Si substrate. 2.6 wt% polystyrene (PS) nanospheres aqueous solution with the diameter of 465 nm were purchased from commercial company (Polysciences, Inc.). The original PS solution was first diluted with an identical volume of ethanol, and then dropped onto a large Si wafer assembling with a monolayer of dodecylsodiumsulfate molecule, subsequently forming large-scale closely packed monolayer PS nanospheres array. The PS array was lifted off from the Si wafer and floating on the surface of the water due to the hydrophobic effect. Finally, the PS array was transferred to another clean Si substrate for the following processes, as shown in Figure 3.6. The sample substrate was successively cleaned using acetone, ethanol and purified water in an ultrasonic bath at room temperature. The sample was then mounted into the vacuum chamber of electron-beam deposition system and gold film of 50 nm thickness was deposited onto the substrates. Finally, the nanospheres were removed by sonicating the entire substrate in dichloromethane (CH₂Cl₂) for 1 minute. The morphology of sample was characterized by field emission scanning electron microscopy (FE-SEM, JEOL

JSM-6700F).

Figure 3.6: Fabrication processes of Au nanoparticles array on Si substrate using nanosphere lithography (NSL).

3.2 Scattering and photoluminescence measurements

3.2.1 Dark field scattering spectroscopy in reflection mode

Optical property of single noble metal nanoparticle is always one of fundamental interests, providing basic insight into complex plasmonics. As one of resonance characterization techniques, dark field Rayleigh scattering spectroscopy is powerful, efficient and common method to obtain plasmon resonance of single metal nanoparticle. Moreover, some useful information, for example, the plasmon damping mechanism and life time, could be achieved from their scattering spectra.^{11, 12}

Figure 3.7 (a) Optical image of dark field microscope developed from WITec confocal Raman system using special dichroic mirror and dark field objective lens. The correlated optical path diagram in (b) is list as below: ① White light source (Halogen); ② Mirror step assembly; ③ Mirror with a hole; ④ Objective lens.

Our home-made dark field microscope, as presented in Figure 3.7, was developed from a WITec CRM200 confocal Raman microscopy system. A halogen lamp (15 V 150 W, 3150 K) was chosen as the white source and illuminated the sample *via* a dark field objective lens (Zeiss Epiplan, 50x, N.A. =0.5, 100x, N.A. = 0.75 or 0.9), which was also used to collect the scattered light. The white light source could be polarized along either horizontal or vertical directions by broad band polarizer. The scattering spectra were dispersed by 150 lines/mm grating and detected using a TE-cooled CCD (Andor DV 401-BV-351). High resolution spectrograph (0.55 nm/pixel) allows peak positions of scattering to be accurate within ± 1 nm.

For dark-field scattering measurement of individual Au nanostructure, a 3 dimensional piezoelectric stage(x, y and z) was used to approach the maximum scattering intensity. The integration time for scattering spectra was set as 20s. In our experiments, for all of the scattering spectra presented, contributions from substrate scattering were excluded. The final results were normalized with the light source spectrum and the response curve of the entire optical system using WITec project 2.4. The details of calculation are described in the formula below:

$$I_{scat}(\lambda) = \frac{I_{particle} - I_{sub}}{I_{Halogen} - I_{dark}}$$

where $I_{scat}(\lambda)$ is the real scattering spectrum of single nanoparticle; $I_{particle}$ and I_{sub} are the original scattering spectra collected from nanoparticle and adjacent substrate without nanoparticle, respectively. $I_{Halogen}$ and I_{dark} are the spectrum of the halogen light source and the background count of our system, respectively.

3.2.2 Correlated single photoluminescence measurement in far field

For PL measurement, linearly polarized green laser with the wavelength of 457 or 532 nm was selected as excitation source and focused on the individual plasmonic nanostructure *via* the same Zeiss Epiplan objective lens as scattering measurements. The Nd:YAG green laser was purchased from CNI. The laser power was set as 50 μ W to excite the PL. All PL spectra were obtained with an integration time of 20 s. A piezoelectric stage was used to approach the maximum luminescence intensity. The photoluminescence spectra under parallel and perpendicular polarizations (0 and 90 degrees) were achieved by manually rotating the sample. An analyzer was placed after the objective lens to record light polarized along the 0 or 90 degrees.

To verify whether the obtained PL spectrum is one photon process, we normally investigate the PL intensity as a function of the excitation laser power.

3.2.3 Comparison between scattering and single photoluminescence

Here I briefly present the fundamental differences between scattering and photoluminescence from several important aspects, for instance, the light source, incident direction and post-treatment. It is worth noting that all photoluminescence and scattering spectra shown in thesis were recorded using the same setup. The plasmon resonances of plasmonic nanostructures were characterized by dark field microscopy prior to the PL measurements. Figure 3.8 represents the schematic diagrams of dark field scattering (a) and photoluminescence (b) measurements. In dark field scattering, the Au nanostructure was illuminated with a broadband white light at glancing incidence, as indicated in Figure 3.8a. The elastically-scattered light

as marked by colorful wavy arrow was collected by an objective positioned above the sample. The scattering spectra presented in thesis have been normalized with the light source, CCD response and instrument dark current. In the photoluminescence setup, we only used a linearly-polarized monochromatic laser ($\lambda=457$ or 532 nm) to excite the photoluminescence of metal nanostructures at normal incidence. There is no post-treatment for PL spectra.

Figure 3.8: Schematic comparisons of optical excitation and collection for dark-field scattering and photoluminescence. Single gold nanodisk fabricated by EBL on 100 nm thick SiO₂ dielectric on Si substrates was taken as a typical example. (a) In dark field scattering, a broadband light introduced at glancing angles is elastically scattered and subsequently collected by an objective lens. The most intense scattering occurs at the plasmon resonance condition of the nanostructure. (b) In photoluminescence, a continuous wave (CW) excitation laser with the wavelength of 457 or 532 nm was introduced normal to the substrate, and induces inelastic processes within the nanostructures. The Stokes-shifted photoluminescence from the nanostructures was collected.

3.2.4 Photoluminescence measurement in near field

It has been extensively demonstrated that scanning near-field optical microscopy (SNOM) through near-field excitation or collection could provide important information, which completely decays within sub-wavelength region. In order to obtain the near-field intrinsic photoluminescence of plasmonic nanostructures, one aspect, plasmon coupling between sample and near field probes, should be taken into account. It is obvious that noble metal AFM or STM tips are not suitable to apply for PL spectrum or imaging due to the strong plasmon coupling.¹³ However, for normal aperture SNOM technique, low efficiency makes it impossible to obtain near-field PL image of plasmonic nanostructures with $\sim 10^{-6}$ quantum yielding. Recently, a novel near field technique with subwavelength spatial resolution has been established from dielectric microsphere due to photonic nanojet. Such method has been utilized to collect near field Raman spectra of a doped SiGe transistor, demonstrating good Raman imaging with ~ 80 nm spatial resolution. More importantly, there is no plasmon involvement for dielectric microsphere. Therefore, in Chapter 6, I will present the near-field plasmon-enhanced photoluminescence image visualized through optically trapping dielectric microsphere.

Scanning near-field PL measurements are performed on WITec CRM200 confocal Raman Microscopy system (25 μm pinhole) with OLYMPUS water immersion objective (60x, N.A. =1.2), as shown in the schematic diagram in Figure 3.9. To avoid the interference of other un-trapped spheres during mapping, the polystyrene (PS) microspheres with diameter of 1 μm that were purchased from

commercial company (Polysciences, Inc.) were drastically diluted with purified water. Then the diluted PS aqueous solution was dropped into a prepared square hole on a large aluminum plate, where the measured sample was adhered by conductive carbon tape. A thin cover glass was placed over the aluminum to prevent the sample and PS from outside. A linearly polarized 532 nm green laser was used to trap single PS sphere, deliver the incident light to sample surface, and collect near field PL signals. The PL images were achieved via point by point with 40 nm step size. The excitation polarization was adjusted using a half-wave plate before objective lens.

Figure 3.9: (a) Schematic illustration for near-field PL measurements using dielectric microsphere.

(b) The details of the sample cell: 1. 60x water immersion lens; 2. 532 nm green laser; 3. Water; 4. Cover glass; 5. 1 μm polystyrene microsphere; 6. Sample; 7. Liquid cell.

3.3 Numerical simulations

Theoretical analysis of particle plasmon of metal nanostructures have been achieved by solving out Maxwell's equations with special boundary conditions. The basic principle is to treat noble metal as wavelength-dependent dielectric materials. Thanks to the numerous efforts by pioneers, there are several well-developed methods for any arbitrary shape and size, for example, discrete dipole approximation (DDA),^{14,}¹⁵ finite element methods (FEM)^{16, 17} and finite-difference time-domain (FDTD)^{18, 19}. In this thesis, a 3-dimensional commercial FDTD software (Lumerical Solutions 7.5, Inc.) was used for electromagnetic simulation, providing deeper understanding of our observations. A brief introduction of common FDTD method will be summarized here.

In 1961, K.S.Yee proposed a new mathematical solution to solve the Maxwell equations using Taylor expansion.²⁰ Naturally, FDTD is mainly involved with the following two time dependent equations derived from Maxwell equations.

$$\nabla \times \vec{E} = -\mu(\vec{r}) \frac{\partial \vec{H}}{\partial t} \quad (3-1)$$

$$\nabla \times \vec{H} = \sigma(\vec{r})\vec{E} + \varepsilon(\vec{r}) \frac{\partial \vec{E}}{\partial t} \quad (3-2)$$

Here, $\varepsilon(\vec{r})$, $\sigma(\vec{r})$, $\mu(\vec{r})$ are the dielectric constant, electric and magnetic permittivity of materials, which are dependent upon spatial position $\vec{r}$.

Figure 3.10: Schematic model of a standard Yee cell for FDTD simulation in a Cartesian coordinates, showing the spatial distribution of the electric and magnetic field vector components. Note that the electric field components were assumed to be at the edges center of the cube, while the magnetic field components were located normal to the cube faces.

The basic FDTD algorithm is to create discretization in time and space domain, where the electromagnetic field and materials are represented by a discrete Yee cell. As shown in Figure 3.10, the electric field ($\vec{E}$) is shifted by half-grid points with respect to magnetic field ($\vec{H}$). The electric field components are assumed to be at the edges center of the cube, while the magnetic field components are located normal to the cube faces. Each electric component is enclosed by four magnetic components and vice versa, forming a direct spatial correlation of field circulations. Taking a 2-dimensional system as example, electromagnetic field components at certain time step t could be described as the following derivatives.

$$\begin{aligned}
 E_x^{n+1/2} &= E_x^{n-1/2} + \frac{t}{\epsilon} \left(\frac{\partial H_z^n}{\partial y} - J_x^n \right) \\
 E_y^{n+1/2} &= E_y^{n-1/2} - \frac{t}{\epsilon} \left(\frac{\partial H_z^n}{\partial x} + J_y^n \right) \\
 H_z^{n+1} &= H_z^n - \frac{t}{\mu} \left(\frac{\partial E_y^{n+1/2}}{\partial x} - \frac{\partial E_x^{n+1/2}}{\partial y} \right) \quad (3-3)
 \end{aligned}$$

Fourier transforms are used to calculate the response of materials in frequency domain from time-domain solutions. So far this method has been fully developed to be the state-of-the-art technique, providing 2- or 3- dimensional information within time and frequency domains for all type of electromagnetic systems, especially for optical properties of plasmonic nanostructures.²¹⁻²³

3.4 References

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Chapter 4

Plasmon-Modulated Photoluminescence of Individual Gold Nanostructures

4.1 Introduction

In addition to producing strong localized electric fields,¹⁻³ resonant plasmons in noble metal nanostructures are also responsible for the absorption of photons to create excited or hot electrons in the metal.⁴⁻⁶ These properties are of great importance in light-matter interactions, in particular, to enhance the spontaneous emission of semiconductor nanomaterials⁷ or molecules⁸. Interestingly, the inverse process, namely, of generating photons from non-equilibrium electrons in metal nanostructures themselves, can be facilitated by resonant plasmons as well. The efficacy of this resonant effect has been observed in the photoluminescence (PL) of gold nanoparticles being several orders of magnitude larger than in the bulk film.⁹⁻¹² Consequently, PL in gold nanoparticles has been ascribed to the radiative damping of particle plasmons generated by the recombination of *sp*-band electrons and excited *d*-band holes.¹⁰ However, some doubt remains in the involvement of plasmons in the PL process,¹²⁻¹⁵ and an agreement in a mechanism for the PL process in nanostructures is lacking.

In this work, we performed a comprehensive study correlating PL with dark-field scattering spectra of individual lithographically-defined Au nanostructures of different geometries and sizes. Detailed analysis on the PL peaks, absolute intensities and

linewidths of the gold nanostructures was done. The spatial distribution of the nanodisk's emission (depolarization effect) was studied. Theoretical simulations by FDTD were conducted to confirm experimental results. A simple plasmon-modulated PL model and approximate expression of PL spectral feature were proposed based on our observations.

4.2 Sample preparation and optical measurements

To systematically investigate the photoluminescence of Au nanostructures and the role of surface plasmons, we fabricated a set of Au nanostructures with different shapes, sizes, and gap sizes by electron-beam lithography (EBL). The thickness of Au nanostructure was 30 nm with a 1 nm Cr adhesion layer. A gold film was also fabricated on the same sample as a reference for PL measurement (see *Chapter 3* for fabrication details).

The plasmon resonances of Au nanostructures were characterized by dark field microscopy prior to the PL measurements. In dark field scattering, the Au nanostructure was illuminated with a broadband white light at glancing incidence. In the photoluminescence setup, a linearly-polarized green laser ($\lambda=532$ nm) was mainly used to excite the photoluminescence of Au nanostructures at normal incidence. Other excitations by different lasers were used to further confirm the photoluminescence. In our experiments, the photoluminescence and scattering spectra were recorded using the same setup with the only difference being the excitation source and illumination angles. Details about the optical measurements of scattering and photoluminescence spectra and their analyses are in the section 3.2.

4.3 Results and discussions

4.3.1 Shape dependent photoluminescence

Figure 4.1: Shape dependent photoluminescence (PL) of single Au nanoparticles. (a) SEM images of the single Au nanodisk, nanotriangle and nanorod used in the measurements. (b, c) Corresponding dark field scattering spectra and PL spectra of these particles, respectively, color coded to the particular nanostructure shape. The excitation wavelength for PL was 532 nm. The green arrow in (c) indicates the Rayleigh scattering of the laser, while the sharp peaks marked by the red stars belong to the first- and second-order Raman scattering of the SiO_2/Si substrate. (d) Plot of peak position and FWHM for different geometries showing the close correlation between PL (red) and scattering (black) spectra in (c) and (b). (e) i-iii: PL/scattering ratio of the three nanoparticles, showing similar profiles and trends as the PL spectrum of an unpatterned Au film (iv), suggesting a link between film PL and PL/scattering ratio of nanostructures as described in the chapter.

It is well-known that shape of noble metal nanoparticles even with identical dimensions could give rise to totally different plasmon resonances. To our best knowledge, there is no report about the relationship between PL emission and metal nanoparticles' shapes. Here we mainly investigate the dark-field scattering and PL of single Au nanoparticles with three different geometries. Figure 4.1a shows SEM images of the nanodisk, nanotriangle and nanorod. With the help of registration marks (Figure 3.3 in chapter 3), we were able to precisely collect the scattering and PL spectra from the exact Au nanostructures as imaged in the SEM. Both the white light source and excitation laser were polarized along the horizontal direction. In Figure 4.1b, we see that these three types of nanoparticles in scattering spectra show clear plasmon resonances with peaks at 596 nm (disk), 634 nm (triangle) and 661 nm (rod). When excited by a 532 nm laser, these nanoparticles showed an obvious shape-dependent PL with peaks appearing at 588 nm (disk), 621 nm (triangle) and 653 nm (rod), as illustrated in Figure 4.1c. To avoid other possible origin of these broad peaks, for instance, Raman signals, we checked the PL spectra of 80 nm Au nanodisk excited by other lasers with different wavelengths of 457, 488, 514 and 633 nm, as shown in Figure 4.2. Obviously, we still can observe these broad spectra with the almost same peak at 588 nm, further confirming the reality of PL from Au nanoparticles and also revealing independence of the laser wavelength.

Figure 4.2: PL spectra of single Au nanodisk with 80 nm in diameter excited by different lasers with the wavelength of 457, 488, 514, 532 and 633 nm. Note that all of them except for 633 nm excitation show almost identical PL peak at 588 nm, suggesting that the optically excited electrons in spite of different energies could decay to the same plasmon energy level.

Close correlations in peak positions and spectral linewidths between the PL and scattering spectra, as shown in Figure 4.1d, suggest the dominant role of plasmon resonances in the generation of photoluminescence. The shift of plasmon resonances due to changing nanostructure shape was closely tracked in the resulting PL spectra. It is therefore unlikely that photoluminescence arose solely from the direct recombination of *sp* electrons and *d* holes,^{14, 16, 17} as such a direct recombination would result in spectrum that was shape independent, and depended only on material

and temperature. On the other hand, the broad peaks in plasmon resonances as measured by their linewidths are known to originate from photon emission (radiative damping) and absorption (dephasing or nonradiative damping).^{18, 19} Hence the match in linewidth between PL and scattering from these nanostructures suggests that the PL process indeed occurred *via* plasmon generation, hence sharing the same damping mechanism.

We observed that the photoluminescence peaks were consistently blue shifted (~ 10 nm in wavelength) with respect to the scattering peaks, as illustrated in Figure 4.1d. We have carefully investigated the origin of this blueshift to ensure that it is reproducible, and not due to the effect of varying excitation-collection angles²⁰ in dark field microscopy. We observed no dependence on collection angle in scattering spectra collected using objective lenses with different numerical apertures (N.A. = 0.5, 0.75 and 0.9, see Figure 4.3). We also show that the blue shift in PL relative to scattering spectra was systematically larger than the slight shifts that could result from differences between absorption and scattering cross sections, which are less than 8 nm as shown in Figure 4.4. The following spectral analysis offers a possible explanation to this blue shift. Note that the relative peak intensities for PL of $I_{disk} > I_{triangle} > I_{rod}$ are different from those in scattering where $I_{disk} > I_{rod} > I_{triangle}$. However, it is surprising that the ratios of PL to scattering spectra exhibit similar profiles for all three nanostructures, as shown in Figure 4.1e(i-iii). More interestingly, those profiles closely resemble the photoluminescence spectrum of bulk Au film as shown in Figure 2e(iv), which is known to arise from the thermalization of photo-excited

non-equilibrium electrons in the absence of particle plasmons.^{13, 16} The resemblance can be rationalized by considering that this “material dependent” thermalization process occurs in nanostructures in the same way as in an unpatterned film, presumably before the electrons excite particle plasmons. Thus, taking the ratio of PL to scattering spectra intuitively normalizes out the contribution of the plasmon antenna scattering strength from the PL spectra and provides a distribution of the non-equilibrium electrons available for the excitation of plasmons that lead to PL emission. Thus, this admittedly simple analysis suggests that the blue shift of the observed PL could be due to the higher availability of excited electrons closer to the initial energy of the laser excitation. To validate this hypothesis, further solid-state theoretical calculations and experiments are needed.

Figure 4.3: Scattering spectra of single 80 nm Au nanodisk obtained under three different dark field objective lenses (N.A.=0.9, 0.75, 0.5), ruling out the possibility that the blue shift between photoluminescence and scattering is induced by geometric effect of dark field microscopy.

Figure 4.4: (a) FDTD Simulated extinction cross section of individual Au nanodisk with the correlated diameter with the case in Figure 3. (b) The simulation results show obvious increase in photon absorption efficiency for 532 nm laser with increasing the disk diameter. (c) The peak positions of measured scattering (black), PL (blue), and simulated scattering (red), extinction (green) spectra, further confirming the shift of PL peak with respect to the plasmon resonance one.

4.3.2 Size dependent photoluminescence

We now present another important plasmon effect on PL, *i.e.*, the size of nanostructures. Scattering and PL measurements were done on single Au nanodisks with diameters ranging from 60 to 140 nm, as shown in Figure 4.5a. The corresponding scattering and PL spectra are illustrated in Figure 4.5b and 4.5c, respectively. As seen in Figure 4.5b, increasing the diameter of the nanodisks, both intensified and red shifted the plasmon resonance, as expected. The corresponding PL spectra are displayed in Figure 4.5c, showing similar size dependence with scattering spectra. The blue shift of PL peaks was also reproducibly observed here as it was in Figure 4.1. From Figure 4.6, we can see that the ratio of PL/Scattering spectra of nanodisk with different sizes shows similar profiles and tendency as those in Figure 4.1e due to the thermalization effect. Simulation results for the corresponding structures are shown in Figure 4.5d, with excellent agreement shown in Figure 4.5e together with the blue shift of the PL peaks.

Figure 4.5f shows the different trends in the PL and scattering peak intensities. The absolute PL intensity was highest for the 80 nm nanodisk, while the scattering intensities showed a monotonically increasing trend. This decrease in PL for larger nanodisks is rather surprising, for two reasons: (1) the larger nanodisks are better scatterers, and so should more strongly reradiate the absorbed light through PL, and (2) they absorb more of the laser light due to their larger absorption cross sections (see simulation results in Figure 4.4), which should also provide more energy for PL. The reason for the decrease in PL can be explained by considering the energy mismatch between the excitation laser and the PL peak. With larger nanodisks, the PL peak occurs at longer wavelengths where there are fewer non-equilibrium electrons to excite plasmons. To illustrate this point, we first normalized the PL intensity by scattering intensity taken at the different PL peak energies, similar to what was done in Figure 4.1e, and obtained the plot shown in Figure 4.5g. When plotted as a function of the energy difference between the excitation and PL peak energy, ΔE , we indeed observe that the amount of excited plasmons decreases monotonically when the energy match between excitation and plasmon resonance becomes poorer. It is satisfying to see a connection between this trend and that of the PL spectrum in Figure 4.1e. The resemblance simply reflects the fact that the non-equilibrium electrons are more highly populated at energies closer to their initial excited states, *i.e.*, at small ΔE , hence leading to higher PL intensities as there are more available non-equilibrium electrons to excite plasmons.

Figure 4.5: PL of Au nanodisks with different sizes to demonstrate dependence of PL intensity on energy mismatch between excitation laser and plasmon resonance. (a) SEM images of the single Au nanodisks with different diameters from 60 to 140 nm. (b, c) The dark field scattering and PL spectra of the particles in (a), showing size dependence. (d) Numerical simulation of scattering spectra using finite-difference time domain (FDTD), closely matching experimental results. (e) The peak positions of measured (black), simulated (red) scattering and PL (blue) spectra, indicating the correlation between PL and plasmon resonance. (f) The scattering (blue curve) and PL (red curve) intensities as a function of the particle size. (g) A plot of the PL/scattering ratio at the PL peak position of each particle as a function of the energy mismatch (ΔE) between excitation laser and the plasmon resonance energies.

Figure 4.6 Ratio of PL/Scattering spectra of individual nanodisks with different diameters, showing similar profiles and trends as the PL spectrum of bulk Au film in Figure 4.1e. The resemblance further confirmed the existence of thermalization process, giving rise to blue-shifted PL emission.

4.3.3 Spatial distribution of photoluminescence (depolarization effect)

To obtain insight of the depolarization process of the incident photons caused by the thermalization of photo-excited electrons, we investigated the excitation and collection polarization dependence of the PL spectra in terms of peak intensities. A symmetric nanodisk was selected as an example for this study. Two different excitation polarizations (0° and 90°) were used, and the PL was collected also in two different configurations: 0° and 90° direction. From Figure 4.7, we see that, under parallel (0° - 0° and 90° - 90°) or orthogonal (0° - 90° and 90° - 0°) configuration, the almost identical polarized PL spectra indicate independence on the excitation

polarization, which confirms that the incident photons lost their polarization during photoluminescence process.

Figure 4.7: (a) Excitation polarization dependence of the photoluminescence spectra from single 80 nm diameter symmetric Au nanodisk as shown by the SEM image. The nanodisk shows incomplete depolarization where PL emission occurs preferentially in the same polarization as the excitation (*i.e.*, red and green lines have higher intensities than blue and pink lines). The excitation and collection polarization angles relative to the structure are indicated by the blue arrows. In contrast, the right panel shows near identical scattering spectra of the nanodisks for two orthogonal white light polarizations, as shown in (b). The simulation electric field distribution under 532 nm laser excitation is presented in (c). The spatial location of energetic electrons along the laser polarization direction attributed to the preferential PL emission at that direction.

The complete depolarization of photo-excited electrons due to fast thermalization in PL is well-known in single Au nanorods^{11, 12} and colloidal Au nanospheres¹³, accounting for the independence of PL on polarization of the laser excitation. In other words, once a photon is absorbed, all “memory” of the polarization of the photon is

lost. However, as demonstrated using the symmetric nanodisk in Figure 4.7, we surprisingly found that the emitted light (through radiative damping of plasmons) had a tendency ($\sim 25\%$ higher in this particle) to be polarized in the same direction as the incident light. This preferential PL from the same excitation polarization suggests incomplete depolarization of the incident light in the processes prior to plasmon excitation and radiative damping. To avoid the possibility of preferential scattering in any particular direction, we measured scattering spectra at the two orthogonal polarization directions and obtained identical scattering intensities, as shown in Figure 4.7b.

One hypothesis for this incomplete depolarization is that the non-equilibrium electrons are not uniformly distributed within the disk, but are instead localized in the regions of the highest laser field intensities. From the simulated electric field distribution in Figure 4.6c, the continuous wave (CW) green laser (532 nm) creates strong localized electric fields along the opposite edges of the disk along the direction of the laser polarization. These are the edges where electrons are preferentially photo-excited due to the stronger electric fields present. Given that the disks are larger than the electron mean free path ~ 50 nm,²¹ the excited electrons could remain non-uniformly distributed within the disk even after thermalization. Now, as we have learnt from electron energy-loss spectroscopy (EELS),²²⁻²⁴ the position of the electron beam determines the plasmon resonance modes that are excited, with modes having stronger electric fields in the path of the beam being favorably excited. Analogously in PL, non-equilibrium electrons would preferentially excite plasmons that have a

high electric field distribution right where these electrons are localized. In this particular case, the favored plasmon resonance mode would have a similar field distribution as that shown in Figure 4.6c, which is along the polarization of the laser. Hence the incomplete depolarization arises due to the non-uniform distribution of non-equilibrium electrons in the disk.

4.3.4 Mechanism of Plasmon-modulated PL

To provide a visual picture for the plasmon modulated PL of gold nanostructures, a simple mechanism diagram is given in Figure 4.8, in which the whole PL process is described by four steps as indicated by the numbers in Figure 4.8a.

1) Plasmon enhanced excitation of electrons from the ground state to the photo-excited states with energy of 2.33 eV by 532 nm laser.

2) Excited electrons thermalize to form a population distribution in the conduction band due to scattering, leading to a broad and inhomogeneous energy profile of non-equilibrium electrons. This distribution is the reason for the blue shift of PL spectrum with respect to plasmon resonance in scattering. The population of electrons at a certain energy state is a function of the energy difference (ΔE) relative to the initial state, as shown in Figure 4.8b. Larger ΔE having a lower population, as determined by the excited electron dynamics²⁵ and also manifested in the PL spectra from Au film.

3) Thermalized electrons excite particle plasmons resonance. Resonant plasmons provide a large local density of optical states (DOS) that increase the decay rate of the

excited electrons,^{26,27} suggesting that excited electrons have a higher probability of exciting plasmons, in accordance to Fermi's golden rule. This additional path made available to the electrons competes with the direct recombination of these electrons with holes, thus modulating the PL over that of the bulk metal.

4) Radiative damping of particle plasmons into photons, as shown by the red wavy arrow.

Figure 4.8. Proposed mechanism of plasmon-modulated PL of gold nanostructures. (a) Schematic diagram of a mechanism to qualitatively understand the PL of Au nanostructures. The whole process includes four steps: (1) Plasmon enhanced excitation of electrons shown as green arrow; (2) thermalization of excited electrons, shown by a blue dashed arrow; (3) excitation of particle plasmons by non-equilibrium electrons shown by black arrow; (4) radiation damping of plasmon into photon, shown by red wavy arrow. (b) represents population distribution of thermalized hot electrons before the formation of surface plasmon. The probabilities to form plasmon resonance and radiative damping can be represented by dark field scattering spectrum in (c). Note that there is photon emission from

Using this model, we can intuitively estimate the PL spectra by two key processes:

$$\text{PL} \sim \text{population profile of thermalized electrons} \times \text{DOS},$$

where population profile of thermalized electrons that resembles the PL spectrum from the gold film (as schematically shown in Figure 8b) provides a broadband background²⁸ while the DOS which is represented by the scattering spectrum (as schematically shown by Figure 8c) determines the optical environment for the resonant decay of the thermalized electrons. This understanding suggests that plasmons are also excited most probably when (1) a high population of non-equilibrium electrons exists in the metal, and (2) these electrons are localized where the density of optical states for the plasmons are highest. With this simple formula, we can explain our observations of the blue shift of PL spectra and energy mismatch (ΔE) effect on the intensity of PL in Figure 4.1 and 4.5.

4.4 Conclusions

In conclusion, we presented a systematic study on photoluminescence (PL) of individual Au nanostructures, showing that the PL peak position can be modulated by their plasmon resonances. We show dependence of PL on the shape, and size of single Au nanostructures, and for the first time demonstrate PL from plasmon-coupled nanostructures. We report the observation of an incomplete depolarization of PL, and hypothesize that it results from an inhomogeneous distribution of non-equilibrium electrons within the nanostructures. A simple mechanism was proposed to illustrate that PL results from the excitation of plasmon resonances by non-equilibrium electrons. Our results and analysis provide insights into processes that occur in PL of gold nanostructures that have implications also in cathodoluminescence and in the

generation of plasmons in tunnel-junctions *via* hot electrons.

4.5 References

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Chapter 5

Plasmon coupling modulated photoluminescence from metal nanostructures

5.1 Introduction

More and more compelling optical properties, such as electromagnetic induced transparency (EIT),¹ Fano resonances² and optical chirality,³ have been observed from metal nanostructures due to the effect of the coupled plasmon resonances. As described in section 2.2 and 2.3, the plasmon coupling between them is not only able to dramatically shift the resonance frequency and but also generate huge and highly confined electromagnetic field, manifested as the surface enhanced Raman scattering⁴ and amplification of spontaneous emission⁵. Indeed, how to accurately control and comprehensively understand this interaction has already become central to extend the optical application of plasmonic nanostructures.

Could single photoluminescence also be generated from the radiative damping of coupled plasmon modes, rather than intrinsic ones? Such studies could completely confirm if photoluminescence is not originated from the interband transition. Moreover, the photoluminescence spectral features can provide some useful information about the dynamics of optically excited electrons with the involvement of coupled plasmon resonances. Although two-photon luminescence from coupled metal nanostructures has been reported,^{6,7} as far as we know, single photoluminescence of the correlated structure is still lacking.

To obtain a relative comprehensive understanding about the photoluminescence spectral features and mechanism from coupled plasmon modes, we chose two typical plasmonic nanostructures, namely, Au nanodisk dimer and single Ag nanowire/ Al_2O_3 /Au film. The Au dimers with varied gap size from 90 nm to connected were fabricated on Si substrate with 100 nm SiO_2 buffer layer by electron beam lithography. The architecture of nanowire on metal film, shortened as nanowire-film, was achieved by directly dispersing chemically synthesized Ag nanowires on Au film. The details about sample preparation refer to Chapter 3. In this chapter, I will mainly study the photoluminescence of these two coupled nanostructures by correlating with scattering spectrum and discuss its physical mechanism.

5.2 Photoluminescence from Au nanodisk dimer

Figure 5.1: (a) Schematic view of photoluminescence of plasmon coupled nanodisk dimer on SiO_2/Si substrate with controllable gap distance d . (b) Dark field optical and SEM images of nanodisk dimers fabricated by EBL, varying the gap size from 90 nm to connected. Note that

single nanodisk is also included for comparison.

The fundamental understanding about the coupling between particle plasmon was obtained from a very simple model: nanoparticles dimer. To vary gap distance is able to provide a promising way to fine tune the strength of plasmon coupling. Thus, to verify the effect of plasmon coupling, single photoluminescence spectra are collected from Au nanodisk dimers fabricated by EBL as illustrated by schematic view in Figure 5.1a. The optical images and the corresponding SEM images of single Au disk and its dimers are presented in Figure 5.1b, showing vivid colors under dark field microscope. The PL spectra of dimers excited by 532 nm laser were collected using the same optical instrument as that used in Chapter 4.

Figure 5.2: Unpolarized photoluminescence of single 80 nm Au nanodisk and dimers under horizontal and perpendicular polarization excitations. Comparing with single nanodisk (a), both the dimer with 10 nm gap and the connected one show broader photoluminescence spectra in (b) and (c), where it is hard to accurately identify the peak positions.

First, we studied the unpolarized PL spectra of two nanodisk dimers with 10 nm and connected gap and did compare them with that of single 80 nm disk. The unpolarized PL spectra are obtained under parallel and perpendicular excitation

condition to the long axis of dimers, as displayed by black and red curves (0° and 90°) in Figure 5.2. For single nanodisk in Figure 5.2a, we observed strong PL peaks and identical PL intensities due to the plasmon resonance at 587 nm under both two laser polarizations, as discussed in chapter 4. Comparing with the PL of single disk, the spectra of the two dimers with 10 and 0 nm gaps in Figure 5.2b and c exhibited slight weakening in absolute intensities and stronger PL emitted under 90° polarization. Moreover, the PL spectra for the dimer were much broader in FWHM than that of the single nanodisk, making it hard to determine the exact peak positions.

In order to identify the origin of PL in coupling system, we placed a linear analyzer, parallel or perpendicular to the laser excitation polarization, in the collection path. And the polarized PL spectra for nanodisk and dimers were also correlated with their polarized scattering spectra. Figure 5.3 shows results of polarized scattering and PL from an individual, and several coupled 80 nm gold nanodisks with gap sizes from connected to 90 nm. We systematically show the scattering spectra of these structures in Figure 5.3a (horizontal excitation) and 5.3b (vertical excitation), from which the trends for the different resonant modes as reported in previous studies are similarly observed.⁸⁻¹⁰ In brief, in the horizontally-polarized excitation, the dipolar bright mode consistently red shifts when decreasing the gap size, which increases the capacitance of the facing edges of the disks that get cyclically charged. The experimental results show good agreement with scattering spectra simulated by FDTD as presented in Figure 5.4b. The peak at ~550 nm in the connected structure corresponds to a high-energy quadrupolar mode (see Figure 5.4d). Though a low-energy

charge-transfer mode is supported in the connected structure, it was beyond the measurement range of our detectors. In the vertical excitation, the resonant plasmon mode corresponding to charge oscillations along the direction of the excitation leaves the facing edges of the disks uncharged, hence its independence to gap size variation. The optical responses under vertical excitation are theoretically supported by FDTD simulation results, as illustrated by Figure 5.4c.

Figure 5.3: PL and scattering spectra of coupled 80 nm Au nanodisks with varied gap size (shown in the SEM images). (a) Scattering spectra of the structures at horizontally-polarized white-light excitation, showing a consistent red shift of the plasmon peak with decreasing gap size and the appearance of a high-energy plasmon peak in the connected structure. (b) Scattering spectra of the structures at vertically-polarized excitation, with no significant energy shift of the peaks when changing the gap size. (c) The PL spectra of the structures obtained with both horizontal excitation and collection polarization, in which the peaks show exactly same trend as these in scattering spectra with horizontal excitation (a). (d) The PL spectra of the structures obtained with horizontal excitation but vertical collection polarization, in which no peak shift was found, same as the observations in scattering spectra with vertical excitation (b). Note that PL intensity in (c) and (d) are shown at the same scale. The green double arrows indicate the excitation polarization directions, while the red double arrows indicate the collection polarization directions.

The corresponding polarized PL spectra of these structures are measured with fixed horizontal polarized laser excitation but with different collection polarizations. Figure 5.3c and d From Figure 5.3c, it can be seen that the PL spectra collected from dimers along the horizontal polarization are distinct from that of the single nanodisk. Rather, they show the same trend as their corresponding scattering spectra in Figure 5.3a. Hence, the PL along the horizontal direction originated from the coupled bright dipolar modes. In contrast, no energy shift was found in the PL spectra collected in the vertical polarization, resembling the corresponding scattering spectra (Figure 5.3b), as governed by the transverse plasmon resonances. Though the excitation was along the horizontal direction, PL emissions polarized in the orthogonal direction has previously been reported, and is attributed to the dephasing or depolarization of the plasmon and electron scattering events, as discussed later. This set of experiments demonstrates for the first time that PL arising from plasmons in coupled structures follows the resonance shifts of the plasmons. Almost trivially, an argument that PL were solely due to electronic processes within a given nanostructure would be incorrect, as such processes would be unperturbed by the presence of a nearby nanostructure. Rather, the results here provide further evidence that PL is a consequence of the radiation damping of plasmon resonances, with modes that are supported across multiple nanostructures. On the other words, the PL spectrum is able to reflect the damping not only from intrinsic plasmon resonances in single nanodisk but also the coupled plasmon modes (longitudinal and transverse) in dimers. This is also the reason why the unpolarized PL spectra in Figure 5.2b and c show obvious

broadening in spectral width.

Figure 5.4: (a) Simulation results for scattering spectra of single Au nanodisk and dimer with varying gap sizes under horizontal and perpendicular excitations. Good agreement with experiments is observed. (b) The simulated electric field and current density distributions of the connected one under horizontal excitation of 570 nm plane wave, showing the behavior of the quadrupolar plasmon mode.

5.3 Photoluminescence from single Ag nanowire/ Al_2O_3 /Au film

When metal nanoparticles are placed on metal planar film with thin insulator buffer layer, their electrostatic interaction can lead to analogous plasmon coupling to the case of nanoparticle dimer.^{11, 12} Such plasmonic mode due to the coupling between localized and propagating plasmon resonances have been demonstrated to be highly localized within the tiny gap between nanoparticle and film, thus which is also called as gap plasmonic mode. Their optical properties have been thoroughly studied both in theoretical and experimental sides,¹³⁻¹⁵ intensively used in various areas, for example, surface-enhanced Raman signals,^{16, 17} amplifying spontaneous emission,⁵ and identifying the non-local quantum effect¹⁸. Most current studies have concentrated on

the coupling of nanosphere-film but a few theoretical attentions¹³ have been paid on the case of nanowire-film. Very recently, the gap nanocavity of Ag nanowire-Ag film was able to drastically enlarge the spontaneous emission rate of organic dye with 10^3 enhancements.¹⁹ Therefore, in this section, we mainly focus on the optical properties of gap plasmon in wire-film system and the correlated single photoluminescence.

Figure 5.5: (a) TEM cross sectional image of single Ag nanowire deposited on Au film coated with thin Al₂O₃, forming nanowire-film configuration. It shows that Ag nanowire has pentagonal structure with slight truncated corners and one crystal side facet of wire nanowire is lying on Au film. Note that the average thickness of Al₂O₃ is 6.5 nm. (b) Schematic represents the 2-dimensional cross section of this NWOM structure. The size of nanowire is labeled by the lateral length d .

The samples were prepared by dispersing chemically synthesized Ag nanowires²⁰ on Au film coated with thin Al₂O₃. The detailed preparation process has been discussed in Chapter 3. To better understand the plasmonic effect in wire-film system, the cross sectional image of this structure was obtained by TEM prior to collection of scattering spectrum. From Figure 5.5a, we can see that the Ag nanowire with pentagonal shape but slightly truncated corners stayed on the Au film through a

crystal side facet. Thus, the 2-dimensional cross profile of Ag nanowire-Au film structure could be represented by schematics in Figure 5.5b. And the diameters of Ag nanowires were characterized by the lateral length as label by d in Figure 5.5b, which is obtained through SEM in this section. The average thickness of Au and Al_2O_3 film are 60 and 6.5 nm, respectively.

Figure 5.6: (a) Optical bright and dark field images of single Ag NW partially deposited on Au film, showing Ag nanowire with the diameter of 84 nm by the SEM image. (b) The scattering spectra of Ag nanowire on Au and Si substrates are obtained under the excitation of horizontally polarized white light. The pronounced resonant peak at 653 nm in red curve represents the gap plasmon mode. (c) The corresponding single-photon luminescence spectra are collected from Au film, nanowire on Si and Au substrates under 457 and 532 nm laser excitations. The blue dashed lines in (b)-(d) reflect the resonance peak at 653 nm. Note that all the lasers are linearly polarized

normal to the long axis of nanowire.

To clear identify the plasmon coupling in wire-film structure, single Ag nanowire was deposited partially on pure Si substrate and Au film coated with Al_2O_3 , as demonstrated by the optical bright and SEM images in Figure 5.6a. This long nanowire has uniform morphology with the diameter of 84 nm. Interestingly, the correlated dark field image of Ag nanowire under the excitation of horizontal white light shows very remarkable color contrast between these two parts. The strong red color exhibited by Ag nanowire-Au film part could be due to the plasmon resonance at 653 nm, as illustrated by the scattering spectrum in Figure 5.6b. This coupling could be understood using imaging model/mirror, where the dipole oscillation of Ag nanowire induces an imaging dipole with opposite charge distribution in the underlying Au film, resulting in obvious red shift in plasmon resonance frequency. And such resonance is only created on Au film, instead of Si substrate, because of the high polarizability of Au film involved with free electrons.

Figure 5.6c represents the single photon luminescence spectra obtained from Au film (green), Ag nanowire on Si substrate (black) and Au film (red) under the excitation of 457 nm laser. Note that the laser polarization was set normal to the long axis of nanowire. For bulk Au film, the peak around 508 nm originates from the radiative combination from electrons in *sp* bands above Fermi level to the holes in *d* bands below Fermi level.²¹ Although there are some observations of PL from Ag nanoclusters and nanowires in literature reports,²²⁻²⁴ we found that the part of nanowire on Si substrate did not appear any PL signal from radiative damping of its

plasmon resonance and even interband transition. Note that the PL of bulk Ag film due to interband transition has been demonstrated to be from 3.6 to 3.9 eV.²⁵ When the laser is shining on Ag nanowire-Au film, the obtained PL spectrum shows two strong peaks at 512 and 655 nm, respectively. The former should belong to the bulk Au film due to the relative large beam spot size (1 μm) with respect to the wire diameter. And the enhancement for this peak intensity could be induced by the strong local electric field produced by Ag nanowire. Correlating PL with the scattering spectrum of wire-film, we noticed that the additional peak at 652 nm was slightly red-shifted from the scattering one. Note that the thin Al_2O_3 film (8.8 eV in band gap) also cannot produce any luminescence within the visible region. To further check if this new peak is really a PL signal, we collected the PL spectra from the same positions as Figure 5.6c using 532 nm green laser. In this case, as depicted in Figure 5.6d, there is a new peak observed from Ag nanowire-Au film at 645 nm with respect to the PL tail of bulk Au film (green), excluding the possibility of this new peak from any Raman signals of organic molecules used for chemical synthesis. The close correlation between these two PL peaks and scattering peak suggests that the additional peak should be attributed to the radiative damping from this gap plasmonic oscillation. In other words, the optically excited electrons are preferential for decaying into the state of gap plasmon mode and then excite that resonance, subsequently giving rise to the PL emission through radiative damping. And the slight blue shift in PL peak energies, especially excited by 532 nm (8 nm) could be induced by the inhomogeneous population distribution of optical excited electrons after

thermalization. Such first findings provide solid evidence that photoluminescence in Ag nanowire-bulk Au film system could be induced due to the large optical density of state (DOS) of coupled plasmon mode, rather than plasmon resonance of wire and interband transition of bulk film.

To verify the type of this new PL process, we investigated the relationship between PL intensity and laser power intensity. As illustrated in Figure 5.7, the emission intensities under the excitation of 457 (a) and 532 (b) nm lasers showed similar linear increase with the increase of laser power intensity. The fact that slopes were approximately fitted to 1 indicates that the radiative damping from the gap plasmon mode is single photon process.

Figure 5.7: Power dependence of photoluminescence of Ag nanowire-Au film under 457(a) and 532(b) nm excitations, showing that the luminescence is single-photon process.

Figure 5.8: (a) Dark field optical images of the Ag nanowire half deposited on Au film under horizontal and perpendicular excitations, showing obvious polarization dependent scattering color. (b) The corresponding scattering spectra were obtained under horizontal (red) and perpendicular (black) conditions. The strong and sharp resonant peak at 653 nm is due to the plasmon coupling of nanowire-film system. Under perpendicular condition, there are one dominant peak at 514 nm and another weak shoulder at 655 nm. (c) and (d) represent the excitation and collection polarization dependences of PL intensity under 457 and 532 nm lasers, respectively, depicting a good dipole behavior in photon absorption and emission.

Considering that nanowire is typical one dimensional material with anisotropic optical response,²⁶ whether would the plasmon coupling and PL also be anisotropic with excitation polarization? Figure 5.8a presents the optical dark field images of nanowire-film under the horizontal and perpendicular excitation, respectively. Apparently, there is a distinct color change from red to blue, also as demonstrating by the correlated scattering spectra in Figure 5.8b. In the case of perpendicular condition, the scattering spectrum exhibited one dominant resonant peak at 514 and another weak shoulder at 655 nm due to the non-zero vertical component of electric field.²⁷ Such finding suggests that it is anisotropic for the plasmon coupling between nanowire and film, namely, occurring only when electric field is perpendicular to long axis.

Figure 5.8c elucidated the effect of laser excitation polarization on the corresponding photoluminescence of nanowire-film structure. Under both 457 and 532 nm laser excitations, we obtained the maximum intensity for the PL regarding the gap plasmon when the laser polarization was set perpendicular to the long axis of nanowire, namely, 90 degree relative angle between them ($\theta = 90^\circ$). In contrast, in the case of $\theta = 0^\circ$, this PL peak almost disappeared. Obviously, these polarization results are analogous to the behavior of scattering spectrum, which is completely different from the case of Au nanodisk dimer. More details about the association between PL intensity and the angle θ for 457 and 532 nm were plotted and fitted to $I(\theta) = I_0(1 + M\sin^2\theta)$. Note that the parameter M is termed as modulation depth, describing the optical anisotropy for excitation polarization. From the fitting results

($M=1.04$ and $M=0.98$), we can see that the nanowire-film structure shows an obvious dipolar response. At the same time, the PL due to interband transition of bulk Au film were also enhanced under $\theta = 90^\circ$, showing 2~3 times stronger than that under $\theta = 0^\circ$. The enhancement could induced by the excitation of plasmon resonance of silver nanowire individually in the case of $\theta = 90^\circ$.

In order to theoretically understand the polarization response of PL intensity, we carried out 2-dimensional full-wave electromagnetic simulations to obtain the absorption cross section and the charge distribution of gap plasmon mode. In Figure 5.9a, the simulated scattering spectra under parallel and perpendicular excitations show good agreement with our experimental measurement. From 5.9c and d, we can see that the simulated charge distribution of the gap plasmonic mode and electric field component along the y direction suggest strong plasmon coupling along horizontal direction rather than the vertical one, which indeed contributes to the observed PL. Moreover, the excitation polarization dependence of PL could be understood due to the differences of absorption efficiency for 457 and 532 nm photons under parallel and perpendicular conditions, as demonstrated in the corresponding simulated absorption cross sections in Figure 5.9b.

Additionally, the PL emission spatial pattern is another important aspect useful to further understand the physical mechanism. In experimental side, we fixed the laser polarization direction perpendicular to the long axis and placed a broad band optical analyzer on the collection path. Figure 5.8d demonstrated that the relationship between PL intensity and the collection angle, namely, α , which was defined as the

relative angle between polarization axis and laser polarization. From the PL spectra excited by 457 and 532 nm lasers, we found that the PL from gap mode worked as dipolar emitter, generating the strongest emission along with the direction of incident electric field ($\alpha = 0^\circ$) and completely eliminating the emission when rotating with 90° ($\alpha = 90^\circ$). The exact collection angle dependences of PL intensity under 457 and 532 nm conditions were plotted and fitted to $I(a) = I_0(1 + M\cos^2 a)$, showing the gap plasmon resonance excited from optically excited electrons radiated like a dipole. It is very interesting that the PL from gap plasmon mode kept the memory of incident light, emitting towards the same direction. The capability of unique directional emission may suggest the potential application of this nanowire-film structure as coherent sub-wavelength plasmonic light source.

Figure 5.9: (a) and (b) Simulated scattering and absorption spectra of 84 nm Ag nanowire-Au film under parallel and perpendicular conditions, respectively, showing good agreement with our experimental observation. The differences in absorption cross section for 457 and 532 nm photons under these two excitations could cause the anisotropy of photoluminescence intensity from the gap plasmonic mode. (c) The charge distribution of the gap plasmonic mode (653 nm) is simulated by FDTD, exhibiting strong plasmon coupling along the horizontal direction, which is also confirmed by the electric field component along y direction in (d).

Figure 5.10: (a) Dark field optical and SEM images of four Ag nanowires on Au film. These nanowires have uniform red color under the excitation of perpendicular polarized white light. The SEM images show that these nanowires have identical diameter of 88 nm but different lengths ranging from 2.3 to 30 μm . (b) The corresponding scattering spectra of these four wires exhibit strong resonant peaks almost at the same wavelength of 677 nm, indicating that the gap plasmon oscillation is independent upon the length of wire. (c) and (d) represent the correlated photoluminescence spectra of these four nanowire-film structure under 457 and 532 nm excitations, demonstrating the PL peaks at 670 and 658 nm, respectively. The similarity in length independence of PL peak position further suggests the exact PL origin from the gap mode.

To achieve tunable plasmon resonant frequency is always desirable for optical application, especially for surface enhanced Raman/fluorescence spectroscopy^{28, 29} and plasmonic devices^{30, 31}. According to the current literature, the coupling behaviors between metal nanoparticles and metal film could be mainly tuned through varying the thickness of buffer layer,³²⁻³⁴ analogous to the case of nanoparticles dimer. In our case, we investigated the possibility to control the resonance and PL frequency *via*

either long length or diameter of nanowire when the thickness of Al_2O_3 was fixed. Experimentally, we measured the photoluminescence and correlated scattering spectra from several nanowires first, then characterized their diameters by SEM.

Figure 5.10a represents dark field optical images of four selected nanowires, which have almost identical diameters (88 nm) but different long lengths ranging from 2.3 to 30 μm from the correlated SEM images. All the corresponding scattering spectra in Figure 5.10b are very analogous, exhibiting strong resonant peaks at 677 nm. When excited by 457 and 532 nm, as displayed in Figure 5.10c and d, it is observed that the four photoluminescence spectra also showed very close correlation with the scattering spectra. Therefore, we can conclude that the plasmon coupling and photoluminescence of gap plasmon mode in nanowire-film are independent upon the length of wire, which is indeed useful for the other applications in future.

Figure 5.11: Diameter dependence of scattering and photoluminescence spectra of NWOM structure. (a) Dark field and SEM images of a series of Ag nanowires with different diameters from 62 to 92 nm. (b) The correlated scattering spectra obtained under horizontal condition represent obvious red shift with increasing the diameter of nanowire. (c) and (d) reflect the corresponding photoluminescence spectra excited by 457 and 532 nm lasers, showing almost identical trend in peak position as scattering spectra. This close correlation further confirmed the physical mechanism of PL from gap plasmonic oscillation.

Figure 5.12: (a) Simulated scattering spectra of Ag nanowire-Au film with the corresponding diameters in Figure 5.11, showing a good agreement with our experimental results. (b) The comparison of peak position of PL and scattering spectra, demonstrating similar tendency with the change of diameter.

Another investigation was conducted to see the behavior of photoluminescence and scattering spectra with another important parameter, namely, the diameter of nanowire. Figure 5.11a demonstrated the dark field optical images of a series of nanowires with various diameters from 62 to 92 nm, determined by their SEM images. From Figure 5.11b, we can see that the plasmon resonant peak positions in scattering spectra exhibited singular shifting towards longer wavelength with the increase of diameter, which increases the retardation effect of nanowires. The peak positions of corresponding PL spectra excited by 457 and 532 nm depicted similar tendency as that in scattering spectra. The corresponding simulation scattering spectra and the comparison in peak positions of PL and scattering are shown in Figure 5.12, exhibiting good agreement with experimental results. Such results further confirm the physical origin that, in the Ag nanowire-Au film system, the PL is definitely the

consequence of radiative decay of gap plasmonic oscillation due to its large DOS.

5.4 Physical mechanism of PL from coupled metal nanostructures

As discussed in Chapter 4, we have proposed a simple model to describe the plasmon-modulated PL of single gold nanoparticles. Indeed, that model is also appropriate to the PL originating from the radiative damping of coupled plasmon resonances, as demonstrated in Figure 5.13a. Taking Au nanodisk dimer as a typical example, there is a similar four-step process, 1) plasmon-enhanced absorption shown as green arrow; 2) thermalization of excited electrons shown as a blue dashed arrow; 3) excitation of coupled plasmon shown by black arrow; 4) radiative decay of plasmon resonance shown by red wavy arrow. For comparison, we place the last PL step of single nanoparticle in Figure 5.13b. In the case of nanodisk dimer, the non-equilibrium electrons simultaneously convert into longitudinal and transverse plasmon resonances, subsequently emitting photons *via* radiative damping. Indeed, there is no physical difference between single nanoparticle and dimer when taking the exact role of plasmon in PL process into account. Plasmon is able to enhance the light absorption efficiency and provide large optical density of states for electrons relaxation. Therefore, we can still utilize the estimation to understand the photoluminescence in the Ag nanowire-Au film system, where the gap plasmonic mode offered a new decay state with high DOS.

Figure 5.13: Proposed mechanism of plasmon-modulated PL of coupled nanostructures. (a) Schematic diagram of a mechanism to qualitatively understand the PL of Au nanodisk dimer. The whole process could also be described using the same four steps as that in single nanodisk, as shown in (b). The critical difference is the final plasmon state where optically excited electrons go *via* electron-electron or electron-phonon scatterings. For dimer, the obtained PL spectra indicated longitudinal and transverse plasmon resonances, instead of intrinsic particle one, play the dominant roles.

5.5 Conclusions

In this chapter, we mainly investigated the single photon luminescence of coupled plasmon nanostructures. The effect of coupled plasmon modes on single-photon luminescence has been verified for first time through nanodisk dimer and Ag nanowire-Au film structure. For nanodisk dimer, it is found that there were two independent PL peaks due to the radiative damping from longitudinal and transverse plasmon resonances. The former showed the same tendency with the decrease of gap size as the correlated scattering spectra, while the latter almost kept constant like the transverse plasmon. In the case of Ag nanowire-Au film, we first observed a new PL

peak from the gap plasmonic oscillation. This PL, emitting as a dipole, showed strong dependence of excitation and collection polarization. Such findings in the coupled system provide very convincing evidences that PL of plasmonic nanostructures is indeed the consequence of radiative damping of their plasmon resonances supported. Our results also offer very useful information about dynamics of non-equilibrium electrons and energy conversion between electrons and photons, benefiting to the application in plasmon-based detection and light devices.

5.6 References

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Chapter 6

Visualization of plasmon-enhanced photoluminescence from Au nanoparticles array

6.1 Introduction

Now, plasmon-enhanced light-matter interaction is attracting increasingly interest both in fundamental research and in technological applications, including, heat-assisted magnetic recording,¹ non-linear optics,² molecular-level spectroscopy,^{3,4} photovoltaics,⁵ and single-photon detection⁶. Recently, single photoluminescence (PL) of noble metal nanostructures has been observed with million-fold enhancement over bulk film.⁷⁻⁹ This strong enhancement was explained to be due to their own plasmon resonance, which results in drastically increasing the radiative damping of energetic electrons excited by photons. Moreover, the PL studies of metal nanostructures will provide a sight into understanding how plasmon affects the energy transfer between photons and energetic electrons.

Considering the effective volume of plasmon, i.e., within sub-wavelength region,¹⁰⁻¹² the near field PL spectrum or imaging would be of great concern. However, note that most current PL results of metal nanostructures (including our PL results in Chapter 4 and 5) were obtained under confocal micro-PL system, still subject to the far field diffraction limit. To our best knowledge, only a few near field PL works have ever focused on PL spectra of noble metals in near field.¹³⁻¹⁵ B. Pettinger *et al* have observed the concomitant PL emission when they did tip-enhanced Raman scattering (TERS) of probing molecules on Au film with a sharp Au tip.¹³ Meanwhile, M.

Sackrow et al has also employed similar equipment to map out the PL hot spots on smooth Au films, demonstrating nanometer-scale gold islands with very high spatial resolution of 12 nm.¹⁴ In these two cases, the observed PL of Au film showed obvious red-shift with respect to that under far field. However, according to our current understanding of PL spectrum from Au nanodisk dimer and Ag nanowire-Au film (See Chapter 5), the PL emission observed by those two groups should be related to the coupled plasmon modes between probe tip and nanostructures, rather than any intrinsic plasmon resonance of measured samples. Recently, a simple and novel near field Raman microscopy has been developed in our group based on the photonic nanojets of dielectric microsphere,¹⁶ which allows to overcoming the diffraction limit. A 3 μm polystyrene (PS) microsphere was trapped by green laser ($\lambda=532\text{ nm}$) to excite and collect Raman signals. By the laser tweezers, we have successfully achieved two dimensional imaging with 80 nm spatial resolutions. Importantly, it is worth noting that this method is completely excluded from plasmon coupling between near field probe and substrate.

In this chapter, we utilized this easy and fast technique to visualize the plasmon-enhanced PL of Au nanoparticles array prepared by nanosphere lithography (NSL). The near field visualization of the effect of excitation polarization has also been investigated.

6.2 Sample preparation and Near-field measurements

The periodic gold nanoparticles arrays were fabricated on Si substrate by NSL,¹⁷

namely, using 456 nm polystyrene nanospheres as a template, as shown in Figure 6.1a. Briefly, 50 nm Au film was coated on a prepared polystyrene sphere array, which then were removed by sonicating the entire substrate in CH_2Cl_2 for 1 minute. The details about the fabrication process have been described in chapter 3. The morphology of sample was characterized by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F).

Scanning near-field PL measurements are performed on WITec CRM200 confocal Raman Microscopy system (25 μm pinhole) with OLYMPUS water immersion objective (60x, N.A. =1.2), as illustrated by Figure 6.1b. A 1 μm polystyrene microsphere optically trapped by 532 nm green laser was used to achieve near field PL excitation and collection. The PL images were achieved point by point with 40 nm step size. The details about experimental setup were described in chapter 3.

Figure 6.1: (a) Au nanoparticles arrays for PL measurements fabricated on silicon wafer by NSL. (b) Experimental scheme of near-field photoluminescence measurement using polystyrene microsphere as probe optically trapped by green laser.

6.3 Results and discussion

Figure 6.2: (a) SEM image of Au nanoparticles array prepared by NSL. (b) The typical PL spectra of Au nanoparticles array obtained under without and with PS dielectric microsphere, respectively. The green area is related to the Si Raman peak at 520 cm^{-1} . (c) The simulated electric field distribution produced by $1\text{ }\mu\text{m}$ PS dielectric microsphere by FDTD, showing strong photonic nanojet. (d, e) are the corresponding images of Si Raman intensity obtained under without and with PS sphere, respectively. (f) The near field image was obtained by inverting the intensity scale bar in (e), interestingly, showing the Au nanoparticle array as the SEM image.

Figure 6.2a presents the SEM image of Au nanoparticles array prepared by NSL. The nanopattern prepared by NSL is almost uniform except for small area defect labeled with green curve. The corresponding PL spectra excited by 532 nm green laser were collected without/with the existence of trapped polystyrene microsphere, as shown in Figure 6.2b. Both these two PL spectra are very similar and broad, ranging

from 535 to 680 nm, which indeed suggests that there is no plasmon coupling between Au nanoparticles and PS. With PS microsphere, stronger PL signal of Au nanoparticles array has been generated. One reason of this could be due to the enhancement of local electromagnetic field produced by dielectric microsphere,¹⁸ as the simulation result shown in Figure 6.2c, which could raise the photon absorption efficiency of Au nanoparticles. Note that the two sharp peaks (547 and 560 nm) are related to the first- and second-order Raman peak of Si substrate. Herein, to verify the improvement of spatial resolution by PS microsphere, we plotted out the images using Raman intensity of the first-order Si peak obtained without and with sphere. For far-field image, as illustrated in Figure 6.2d, the blurred image fails to discern the intensity differences from Si substrate with and without Au nanoparticles, which results from the well-known far field diffraction limit. When the laser light was delivered through the microsphere, comparing to the far field image, the obtained near field Raman image shown in Figure 6.2e shows not only stronger Raman intensity but also higher spatial resolution. Comparing with the SEM image in Figure 1a, we can see that the bright and dark areas are correlated with bare Si and Au nanoparticles, respectively. Same reason of the PL enhancement discussed above is responsible to the increase of Raman signals from bare Si. When re-plotting Figure 6.2e by inverting the intensity scale bar, we obtained an interesting image as Figure 6.2f, which resembles the SEM image of Au array. Such high resolution is able to visualize some small defects in Au nanoarray, as labeled by green curve in Figure 6.2. Note that the average gap distance between two Au nanoparticles is about 95 nm, suggesting that at

least 100 nm spatial resolutions generated by 1 μm PS microsphere allow us to explore the near field PL spectra of Au nanostructures.

Figure 6.3: (a) and (b) Correlated PL images of Au nanoparticles array obtained under far- and near-field conditions, respectively. The former failed to reveal any useful information about the PL intensity distribution due to the far-field diffraction limit. Strong PL hotspots were clearly visualized in the gap between two nanoparticles, forming periodic distribution along the laser polarization direction. Note that the laser polarization was set along vertical direction, as marked by green arrows, also defined as 90 degrees.

To verify the capability of this method for PL studies, we first compared the near-field PL image obtained through PS microsphere with the far field PL image. The correlated far- and near-field PL images of integral intensities were plotted by integrating the whole spectra ranging from 535 to 680 nm. The polarization of 532 nm laser was set as 90 degrees with the horizon, as marked by the green arrows. From Figure 6.3a, we can see that the blurred far-field PL image showed almost homogenous PL intensities at hexagon Au nanotriangles areas. The diffraction limit

made it impossible to identify the PL spectra at different positions, for example, corners, sides or body. When delivering the light through PS microsphere, we found that the enhanced PL inhomogeneously distributed as shown Figure 6.3b, forming a series of periodic hot spots in horizontal direction. Such near-field PL is completely different from the image of Au nanoparticles array shown in Figure 6.2f. This result suggests that some useful information about PL of Au nanostructures, being averaged within far field region, could be obtained *via* laser trapped dielectric microsphere.

By partially overlapping this PL image with SEM (green array in Figure 6.3b), we noticed that these PL hot spots seem to be just located at gap center of each nanoparticles dimer, whose link was parallel to the laser polarization direction. In contrast, for other dimers along 30 and 150 degrees, weaker PL intensities were produced. Such phenomena are hypothesized to be the consequence of the local electromagnetic field of nanotriangle dimers, which have strong anisotropic optical responses with different polarized illuminations. In the case of parallel condition, the strongest emission may be induced by the large local electromagnetic field due to plasmon coupling in nanotriangles dimers, though the interaction was supposed to be weak. In order to confirm our hypothesis, the analysis of PL intensities at different position and the simulation of electromagnetic field were carried on. Figure 6.4a presents the details about PL intensities at different position plotted along the green dashed arrow in Figure 6.3b, which was parallel to the laser polarization. Importantly, the correlated intensity profile of Si Raman peak was also plotted as position reference labeled as black curve. Just at the center of dimer gap, the PL intensity came

to a maximum value, manifesting as hot spot in Figure 6.3b. When moving away from the center, we observed two PL dips relevant to the dips in Raman intensity of Si, as marked by the purple dashed lines, whose relative displacement is about 250 nm. Such positions indeed are correlated with the center of each Au nanotriangle, where the average center-to-center distance is about 275 nm. Further moving away, there were additional PL shoulders with relative strong intensity, corresponding to the position of side edge. The simulated electromagnetic field distribution of Au nanoparticles array excited by 532 nm laser was carried out using Lumerical FDTD solutions. From Figure 6.4b, we can see that the nanotriangle dimer labeled with the red dashed line shows the field distribution as: corner > side > body, which is correlated with the tendency of PL intensities. This correlation confirmed our conclusion that the PL spectra were enhanced by strong local electromagnetic field. Moreover, in the case of 90 degree excitation, the total field strengths around the gap between nanotriangles exhibited pronounced polarization dependence as: $A > B = C$, manifesting as the near-field PL image in Figure 6.3b.

Figure 6.4: (a) The near-field PL intensity profile (red curve) along the green dashed arrow in Figure 6.3b. The correlated Raman intensity of Si was plotted in black curve as position reference. Strong PL hot spots due to large local electromagnetic field were observed at the gap center of Au nanotriangle dimer. (b) The field distribution of Au nanoparticles array was simulated by FDTD under 90 degrees linearly polarized excitations, confirming our observation of near-field PL image.

To obtain more comprehensive understanding about the plasmon-enhanced PL, we investigated near-field PL spectra and images under other two polarizations. Figure 6.5a and c represent the corresponding PL images obtained with the polarization direction along 0 and 30 degrees, respectively. Under these two conditions, it is similar that stronger PL were observed only along the laser polarizations, forming either obvious zigzag pattern or hot spots along 30 degrees as marked by red arrows, which were attributed to the local electromagnetic field as shown by the FDTD simulation result in Figure 6.5b and d. And the near-field PL spectra were collected from the same position (green circles in Figure 6.4 b and 6.5)

under 0, 30 and 90 degrees, which were also plotted in Figure 6.6. Although there is no obvious spectral difference, the PL enhancement due to plasmon under different polarization was visualized.

Figure 6.5: (a) and (c) Polarization dependent near-field PL images of Au nanoparticle array were obtained under 0 and 30 degrees polarized excitations, respectively. Under these two conditions, stronger emissions were observed from these nanotriangle dimers along the laser polarization direction, demonstrating by the overlapping between PL image and green SEM one. (b) and (d) were correlated to the electromagnetic field distributions simulated by FDTD, showing a good agreement with the near-field PL images and further confirming the PL enhancement by the local field.

Figure 6.6: Typical Near field PL spectra collected from the gap center in Au nanoparticle array under three different polarizations, namely, 0, 30 and 90 degrees, respectively. The maximum PL intensity was obtained when laser polarization was set along the long axis of nanotriangle dimer. The exact collection position was labeled by green circle in Figure 6.4b and 6.5.

6.4 Conclusions

In this chapter, we demonstrated the effect of plasmon on single-photon luminescence of Au nanoparticles array using optically trapped PS microsphere. This method not involving with any plasmon allows us to not only obtain the near-field intrinsic PL images but also compare the PL spectra at different positions with higher spatial resolution (~ 100 nm). We observed that the plasmon-enhanced PL hot spots were generated in the gap center of nanotriangles dimer parallel to the laser polarization direction due to the strong local electromagnetic field, which attributed to the high excitation polarization dependence near-field PL images. Such investigation provides

useful information to obtain deeper insight into the role of plasmon in the generation of photoluminescence in plasmonic nanostructures.

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Chapter 7

Summary and Future Plans

7.1 Summary

In this thesis, single photoluminescence of noble metal nanostructures have been systematically studied, providing solid evidence about physical mechanism of photoluminescence and the role of plasmon resonance in this process. A brief summary will be presented as following.

In Chapter 4, we performed a systematic study on the photoluminescence and scattering spectra of individual gold nanostructures that were designed by electron-beam lithography. We identify the role of plasmons in photoluminescence as modulating the energy transfer between excited electrons and emitted photons. By comparing photoluminescence spectra excited by 532 nm laser with scattering spectra, we observed that the photoluminescence of individual gold nanostructures showed the same dependencies on shape and size as the particle plasmon resonances. It is also found that there was a universal blue shift in the PL peak position with respect to the plasmon resonance, which was caused by the inhomogeneous population distribution of optically excited electrons after electron-electron and electron-phonon scatterings. Moreover, we noticed that PL of single Au nanoparticle emitted preferentially in the same polarization as that of the incident laser. Our results provide conclusive evidence that the photoluminescence in gold nanostructures indeed occurs via radiative damping of plasmon resonances driven by excited electrons in the metal itself. A new insight on the underlying mechanism was proposed including our analysis of a

reproducible blue shift of the photoluminescence peak (relative to the scattering peak), and observation of an incomplete depolarization of the photoluminescence.

Plasmon coupling is one important feature of optical response of noble metal nanostructures. In Chapter 5, we demonstrated the effect of coupled plasmon mode on single photoluminescence in coupled plasmonic nanostructures for the first time. Two typical plasmonic nanostructures were chosen, namely, Au nanodisk dimer and single Ag nanowire/ Al_2O_3 /Au film. In the case of Au nanodisk dimer, we observed that the photoluminescence originated from the radiative damping of longitudinal and transverse plasmon modes, rather than intrinsic resonance of each disk. With decreasing the gap size of dimer, we found that the photoluminescence due to longitudinal and transverse modes showed the same tendency in peak position as that in correlated scattering, which further confirmed that the role of coupled plasmon in the generation of PL.

For single Ag nanowire/ Al_2O_3 /Au film, we obtained strong photoluminescence from the gap plasmonic nanocavity in this nanowire-film structure, showing well correlation with scattering spectra. We also investigated the dependence of excitation polarizations for the PL from gap nanocavity, showing strongest PL intensity when laser polarization was perpendicular to long axis of nanowire. This photoluminescence also exhibited pronounced preference along the laser polarization direction due to dipole emission. Moreover, tunable photoluminescence could be accomplished through only adjusting the diameter of nanowire, instead of nanowire's length. These findings provided more useful information about the mechanism of

coupled plasmon-modulated photoluminescence.

In the chapter 6, we carried out the near-field PL measurements using a technique not involving with plasmon to visualize the plasmon-enhanced PL of Au nanoparticles array prepared by nanosphere lithography (NSL). By this method, we observed that the strong near-field PL hot spots were generated in the gap center of nanotriangles dimer parallel to the laser polarization direction, which was the consequence of strong local electromagnetic field. The near-field PL images were found to be highly dependent upon the laser polarization, showing zigzag pattern for 0 degree and periodic lines for 30 and 90 degrees. Such near-field studies benefit to getting deeper insight into the underlying physical mechanism.

7.2 Future plans

To achieve comprehensive understanding the single photoluminescence of plasmonic nanostructures, some other important aspects should be investigated in our future plans as following:

1) Photoluminescence at low temperature. In chapter 4 and 5, we have demonstrated the significance of thermalization in the PL process, resulting in the consistent blue shift in PL peak position with respect to scattering one. It is well-known that, by cooling the local temperature of plasmonic nanostructures, the electron-electron and electron-phonon scatterings could be drastically reduced.¹⁻³ Therefore, this investigation allows us to better understand the underlying physics of blue shift.

2) Time-resolved photoluminescence. The time resolved single photoluminescence of plasmonic nanostructures will provide useful dynamic information about the conversion from optically excited electrons to photoluminescence. In experimental side, it requires a PL system with extremely high time resolution in ~10 femto seconds, since the dephasing time of plasmon oscillation is very short.^{4,5}

3) Photoluminescence of quantum plasmon modes in metal nanostructures

When the gap size of nanoparticles dimer is reduced down to < 5 nm region, the excited electrons due to plasmon resonance may jump from one particle to another, leading to electron tunneling and drastic change in plasmon resonance frequency.^{6,7} However, one central problem in this area is to identify the plasmon modes regarding electron tunneling. In Chapter 5, we have successfully obtained the single photoluminescence of nanodisk dimers with varied gaps, especially showing the sudden jumping in PL peak for gap size from 10 to 0 nm. Our current results and understanding about PL in coupled nanostructures may allow us to get direct evidence about the quantum effect from photoluminescence spectra.

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