

APPLICATOIN OF PLASMONICS IN ENERGY HARVESTING

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Application of Plasmonics in Energy Harvesting

Thesis directed by Prof. Wounghang Park

This thesis studies the application of plasmonics in solar energy conversion and near field thermal energy harvesting.

The efficiency of semiconductor solar cell is limited by the inability of absorbing photons with energy below the bandgap. By designing plasmonic nanograting with resonance at the absorption edge, ~10% overall absorption improvement is achieved. Both localized and propagating surface plasmon modes are observed in the device. Their interaction, and the influence on overall solar cell absorption performance are studied in details.

In addition, this thesis studies the upconversion materials which can convert unabsorbed near infrared photons by semiconductor solar cells into well absorbed visible photons. By tuning the surface plasmon resonance at the upconversion frequency with silver nanograting structure, the photoluminescence of upconversion material can be improved by 39-fold maximum. The rate equation analysis reveals that the improvement is attributed to roughly 3-fold absorption enhancement and 2-fold energy transfer enhancement with plasmonics.

This thesis also explores the application of plasmonics to enhanced near field thermal radiation harvesting. I designed metamaterial to excite the spoof surface plasmon in the terahertz frequency for strongly enhanced thermal radiation. The FDTD simulation developed from the fluctuation electrodynamics demonstrates several hundredfold enhancement of thermally excited electromagnetic energy in the near field.

To my parents and family

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1 Introduction

1.1 Plasma oscillation

Metal is well known for its good conductivity thanks to the free conduction electrons. The electrons can be modeled as free electron gas uniformly distributed throughout the volume of metal, while the effect of the atomic nuclei and core electrons occupying the lattice sites are taken into account by the effective mass. This is the well-known free electron model of metal. Under certain conditions, the free electron gas may undergo collective oscillation whose quantum is called plasmon.

For quantitative study, let's analyze the case of a slab of metal. The spatial displacement Δx of electron gas towards one side of the sheet causes surface charge density ρ on the metal sheet surfaces. The surface, which the electrons shift to, is negatively charged, while the opposite side is positively charged. The surface charge density calculated from Gaussian's law is $\rho = ne\Delta x$, where n is the electron density, and e is the electron charge. The restoring electric field $E = \rho/\epsilon_0 = ne\Delta x/\epsilon_0$ attracts the electrons back by force $F = -eE$. Here, ϵ_0 is the vacuum permittivity. Applying Newton's second law, we obtain

$$m^* \frac{d^2x}{dt^2} = -eE \quad (1.1)$$

Here, m^* is the effective electron mass. Substituting expression of restoring electric field E into Eq. (1.1) results in

$$m^* \frac{d^2x}{dt^2} + \frac{ne^2}{m^* \epsilon_0} x = 0 \quad (1.2)$$

The solution of this equation has the form $x(t) = x_0 \cos(\omega_p t)$, where x_0 is the displacement at $t = 0$, and $\omega_p = \sqrt{\frac{ne^2}{m^* \epsilon_0}}$. The electrons collectively oscillate with the frequency ω_p , which is called the plasma frequency. It depends on the electron density n and electron effective mass m^* . The electrons oscillation is in the direction of displacement which by definition represents a longitudinal oscillation and thus does not interact with light which is usually transverse. For finite metal geometries, however, the oscillation has transverse component and interact with light strongly. The oscillation frequency differs for different geometries. In the case of flat metal surface in vacuum, the oscillation frequency equals to $\omega_p / \sqrt{2}$. It equals to $\omega_p / \sqrt{3}$ for sphere in vacuum.

1.2 The Lorentz-Drude model of metal

The free electron model discussed in the last section takes only the account of electric restoring field with out damping. In real materials, however, the internal collisions of electrons with lattice vibrations or impurities and the radiation emitted by electron acceleration cause damping effect. H. A. Lorentz developed a comprehensive model incorporating the damping effect known as the Lorentz oscillator model. It models the interaction of electron with nucleus like a spring.

$$m^* \frac{d^2x}{dt^2} + m^* \Gamma \frac{dx}{dt} + m^* \omega_0^2 x = -eE \quad (1.3)$$

Here, Γ is the damping coefficient, and ω_0 is the natural frequency. From equation (1.3), we can derive the interaction of electrons inside a material with external electromagnetic wave, which is characterized by the dielectric function ϵ . The displacement of electrons induced by electric field produces macroscopic polarization per unit volume of $P = nex$. Replacing the variable in equation (1.3) by P, we get,

$$\frac{d^2P}{dt^2} + \Gamma \frac{dP}{dt} + \omega_0^2 P = -\frac{ne^2}{m^*} E \quad (1.4)$$

The relation between the polarization and electric field E is characterized by the susceptibility χ

$$P(\omega) = \epsilon_0 \chi(\omega) E(\omega) \quad (1.5)$$

For harmonic electromagnetic field, the susceptibility can be directly extracted from equation (1.4) by performing the Fourier transform over time.

$$(-\omega^2 - i\omega\Gamma + \omega_0^2)P = -\frac{ne^2}{m^*} E$$

Re-arranging the equation above, we get

$$P = \epsilon_0 \frac{\sigma E}{\omega_0^2 - i\omega\Gamma - \omega^2} \quad (1.6)$$

where $\sigma = ne^2/m^* = \epsilon_0 \omega_p^2$. By comparing equation (1.5) and (1.6), it is straightforward to obtain the susceptibility as

$$\chi = \frac{\sigma/\epsilon_0}{\omega_0^2 - i\omega\Gamma - \omega^2} = \frac{\omega_p^2}{\omega_0^2 - i\omega\Gamma - \omega^2} \quad (1.7)$$

Here, ω_p is the plasma frequency we derived in the previous section. From equation (1.7) we can calculate the relative permittivity (also known as the dielectric function)

$$\begin{aligned} \epsilon_r &= 1 + \chi \\ &= 1 + \frac{\omega_p^2}{\omega_0^2 - i\omega\Gamma - \omega^2} \end{aligned} \quad (1.8)$$

In the free electron model of metal, there is no restoring force and thus the natural frequency is zero $\omega_0 = 0$. The relative dielectric function is then given as,

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \quad (1.9)$$

This is the dielectric function of the well-known Drude model. For gold[1], the plasma frequency ω_p equals to $1.35 \times 10^{16} \text{ s}^{-1}$, and the damping coefficient Γ equals to $1.08 \times 10^{14} \text{ s}^{-1}$. The dielectric function is shown in Fig. 1.1 for real part and imaginary part separately. Due to small damping coefficient, the imaginary dielectric function, which corresponds to loss, is close to zero. The real dielectric function changes its sign from negative to positive around the plasma frequency ω_p . At visible wavelengths, the angular frequency ω is much larger than the value of damping coefficient that the Drude dielectric function simplifies to

$$\epsilon_r = 1 - \frac{\omega_p^2}{\omega^2} \quad (1.10)$$

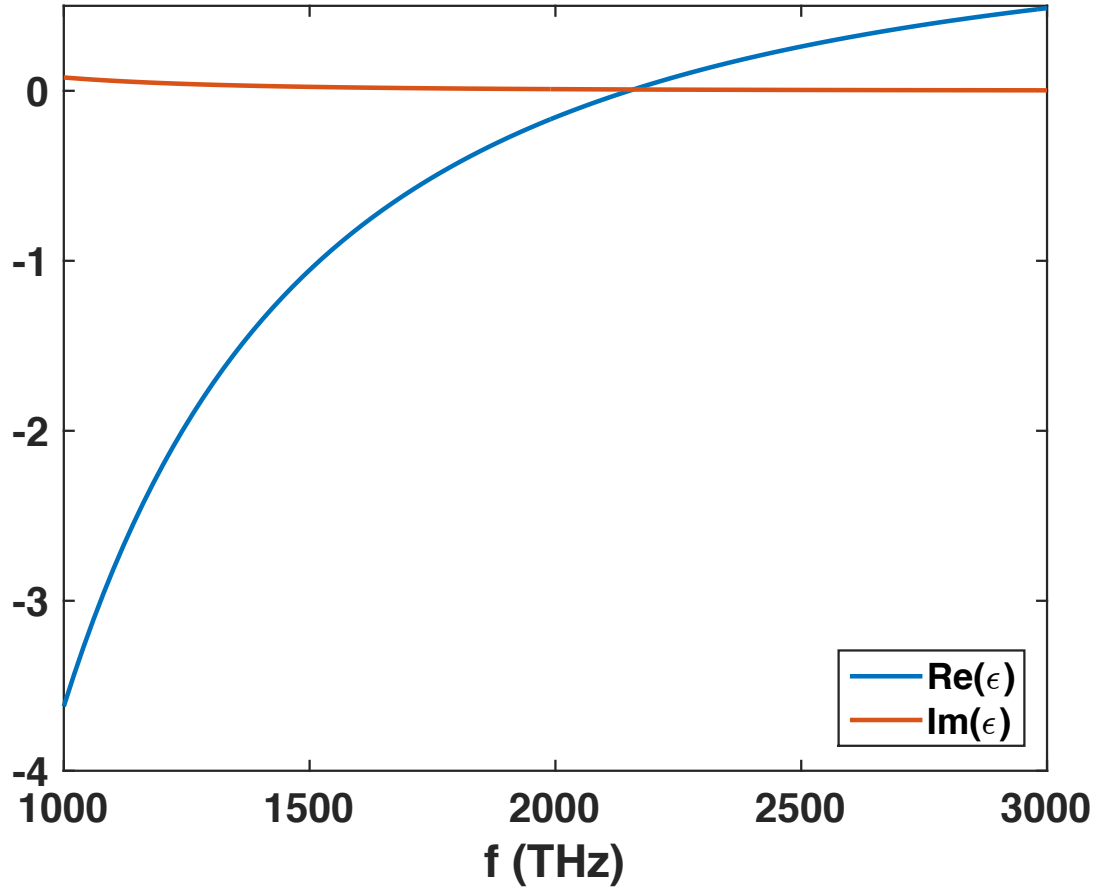


Figure 1.1 The dielectric function of gold from Drude model (1.9) with plasma frequency $\omega_p = 1.35 \times 10^{16} \text{ s}^{-1}$, and damping coefficient $\Gamma = 1.08 \times 10^{14} \text{ s}^{-1}$. The real part and imaginary part are shown in different color.

1.3 Surface plasmon polaritons at planar interfaces

We have derived the bulk plasma oscillation in section 1 of this chapter. It is longitudinal wave by its nature. However, we will see that the surface plasmon, which resides at the interface, is a transvers wave. To derive the surface plasmon formation, we start with the Maxwell's equations:

$$\nabla \cdot \mathbf{D} = \rho_v \quad (1.11)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (1.12)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (1.13)$$

$$\nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \quad (1.14)$$

Here, $\mathbf{D}$ is the electric displacement (unit: C/m²), ρ_v is the free charge density (unit: C/m³), $\mathbf{B}$ is the magnetic flux density (unit: T), $\mathbf{E}$ is the electric field (unit: V/m), $\mathbf{H}$ is the magnetic field strength (unit: A/m), $\mathbf{J}$ is the current density (A/m²).

A constitutive relation accounting for the material response to electromagnetic field is

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathbf{E} \quad (1.15)$$

$$\mathbf{B} = \mu_0 \mu_r \mathbf{H} \quad (1.16)$$

Here, ϵ_0 is the vacuum permittivity with a value of 8.85×10^{-12} F/m, ϵ_r is the relative permittivity, μ_0 is the vacuum permeability with a value of 1.26×10^{-6} H/m, μ_r is the relative permeability. The ϵ_r and μ_r describe the material's response to the external electromagnetic field. They are generally frequency dependent, and can be anisotropic. Take noble metals (Au, Ag, etc.) for example. The relative permittivity is frequency dependent as we can see from Eq. (1.9). The polarization response is independent of incident electric field polarization (known as

isotropic) so that the relative permittivity is a scalar, not a tensor. Also, noble metals are non-magnetic and thus have unity relative permeability μ_r . The units used in this dissertation follow international system of units (SI).

1.3.1 Surface electromagnetic wave

With the Maxwell's equations, we can study the electromagnetic wave on the surface of a metal.

In this case, there are no sources, $\rho_v = 0$ and $J = 0$. First, we derive the wave equation for electric field. The magnetic field can be directly calculated from Eq. (1.14) once we know the electric field. By taking the curl of Eq. (1.13), and substituting Eq. (1.14) and constitutive relations into it, we can obtain the electric field wave equation

$$\nabla \times \nabla \times \mathbf{E} + \mu\epsilon \frac{\partial^2 \mathbf{E}}{\partial^2 t} = 0$$

Re-write it as

$$\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} + \mu\epsilon \frac{\partial^2 \mathbf{E}}{\partial^2 t} = 0 \quad (1.17)$$

For negligible spatial dispersion ($\nabla\epsilon = 0$), the first term in Eq. (1.17) becomes zero based on Eq. (1.11). Then, Eq. (1.17) simplifies to

$$\nabla^2 \mathbf{E} - \mu\epsilon \frac{\partial^2 \mathbf{E}}{\partial^2 t} = 0 \quad (1.18)$$

Assuming harmonic time dependence, $\mathbf{E} = \mathbf{E}e^{-i\omega t}$, Eq. (1.18) becomes

$$\nabla^2 \mathbf{E} + \epsilon_r k_0^2 \mathbf{E} = 0 \quad (1.19)$$

where $k_0 = \omega/c_0$ is the wave number in vacuum. Eq. (1.19) is the well-known Helmholtz equation.

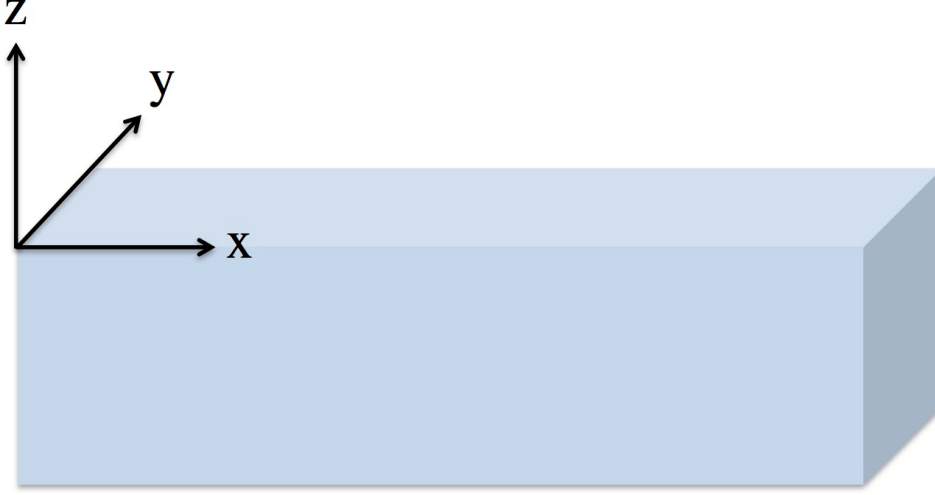


Figure 1.2 Geometry of planar interface of semi-infinite metal (blue) and dielectric (elsewhere).

Now we can solve for the electromagnetic wave at the interface of metal and dielectric (geometry and coordinates shown in Fig. 1.2). The flat metal slab is infinitely large in the x-y plane. The dielectric function ϵ_d is a constant for dielectric material on the top independent of frequency, while it is frequency dependent for metal $\epsilon_m(\omega)$.

$$\epsilon_r(z) = \begin{cases} \epsilon_d & z > 0 \\ \epsilon_m & z \leq 0 \end{cases}$$

The electric field should have the form $\mathbf{E} = \mathbf{E}(z)e^{i\beta x}$ for wave propagating in x direction.

β is the wave number. Substituting the expression of $\mathbf{E}$ into Eq. (1.19), we get

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (\epsilon_r k_0^2 - \beta^2) \mathbf{E}(z) = 0 \quad (1.20)$$

The continuous translation symmetry in the x-y plane leads to two modes: Transverse electric (TE) and transverse magnetic (TM).

$$\text{For TE mode: } \mathbf{E} = \begin{pmatrix} 0 & E_y & 0 \end{pmatrix}, \mathbf{H} = \begin{pmatrix} H_x & 0 & H_z \end{pmatrix}.$$

Substitute the expression of $\mathbf{E}$ into Eq. (1.20), we get

$$\frac{\partial^2 E_y}{\partial z^2} + (\epsilon_r k_0^2 - \beta^2) E_y = 0 \quad (1.21)$$

Looking for an exponentially decaying solution in the upper half space ($z > 0$) we find

$$E_y(z) = A_1 e^{i\beta x} e^{-k_1 z} \quad (1.22)$$

where $k_1 = \sqrt{\beta^2 - \epsilon_d k_0^2}$. Using Maxwell's equation (1.14), we can derive the magnetic field $\mathbf{H}$ from the electric field $\mathbf{E}$.

$$H_x = \frac{i}{\omega \mu_0} \frac{\partial E_y}{\partial z} = -A_1 \frac{ik_1}{\omega \mu_0} e^{i\beta x} e^{-k_1 z} \quad (1.23)$$

$$H_z = \frac{\beta}{\omega \mu_0} E_y = A_1 \frac{\beta}{\omega \mu_0} e^{i\beta x} e^{-k_1 z} \quad (1.24)$$

Similarly, for the lower half space ($z < 0$)

$$E_y(z) = A_2 e^{i\beta x} e^{k_2 z} \quad (1.25)$$

$$H_x = A_2 \frac{ik_2}{\omega \mu_0} e^{i\beta x} e^{k_2 z} \quad (1.26)$$

$$H_z = A_2 \frac{\beta}{\omega \mu_0} e^{i\beta x} e^{k_2 z} \quad (1.27)$$

where $k_2 = \sqrt{\beta^2 - \epsilon_m k_0^2}$.

The tangential components of electric and magnetic fields are conserved at the boundary.

Applying the boundary conditions to E_y and H_x yields

$$A_1 = A_2 \quad (1.28)$$

$$A_1 k_1 + A_2 k_2 = 0 \quad (1.29)$$

For non-trivial solution ($k_1 k_2 \neq 0$), we get $A_1 = A_2 = 0$. Therefore, no TE mode is supported at the interface of metal and dielectric material.

Similar calculation for TM mode: $\mathbf{E} = \begin{pmatrix} E_x & 0 & E_z \end{pmatrix}$, $\mathbf{H} = \begin{pmatrix} 0 & H_y & 0 \end{pmatrix}$. The solved

TM mode field for the upper half space ($z > 0$) is

$$E_x = A_1 \frac{i}{\omega \epsilon_0 \epsilon_d} k_1 e^{i\beta x} e^{-k_1 z} \quad (1.30)$$

$$E_z = -A_1 \frac{1}{\omega \epsilon_0 \epsilon_d} \beta e^{i\beta x} e^{-k_1 z} \quad (1.31)$$

$$H_y = A_1 e^{i\beta x} e^{-k_1 z} \quad (1.32)$$

and

$$E_x = -A_2 \frac{i}{\omega \epsilon_0 \epsilon_m} k_2 e^{i\beta x} e^{k_2 z} \quad (1.33)$$

$$E_z = -A_2 \frac{1}{\omega \epsilon_0 \epsilon_m} \beta e^{i\beta x} e^{k_2 z} \quad (1.34)$$

$$H_y = A_2 e^{i\beta x} e^{k_2 z} \quad (1.35)$$

for the lower half space ($z < 0$).

Apply the boundary conditions (E_x and E_z conserved at the boundary), yield

$$A_1 = A_2 \quad (1.36)$$

$$\frac{k_1}{k_2} = -\frac{\epsilon_d}{\epsilon_m} \quad (1.37)$$

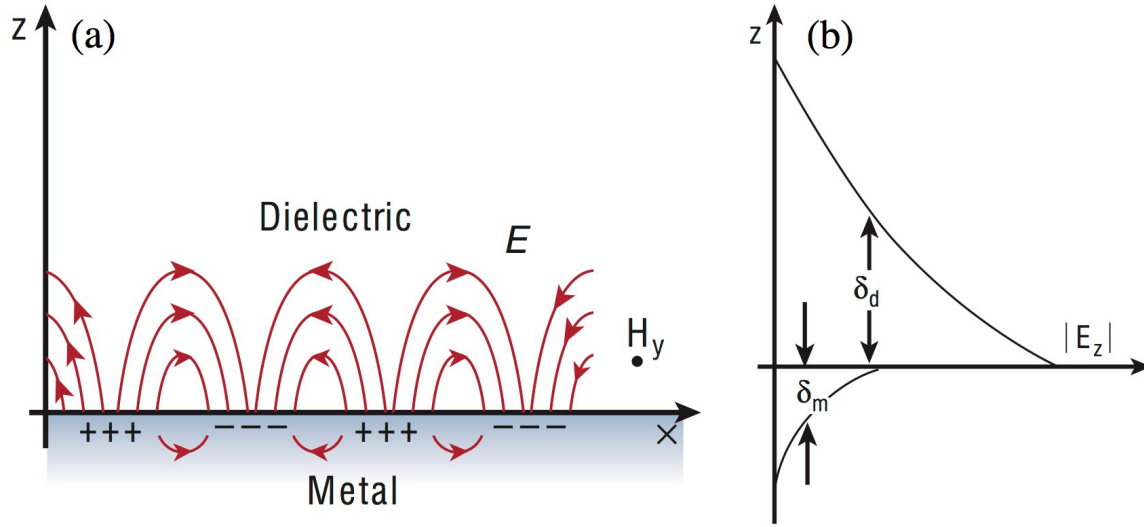


Figure 1.3 Surface plasmon has the combined character of electromagnetic wave and surface charge as shown in (a). The wave is bounded at the interface. The field strength decays exponentially away from the metal-dielectric interface (b). The decay length into the metal, δ_m , is determined by the skin depth, while the decay length into the dielectric, δ_d , depends on the dielectric index. (Ref[2])

Equation (1.37) says that TM surface wave may exist at the dielectric-metal interface only if they have opposite signs of permittivity. For common dielectrics, the permittivity is positive over frequencies of interest. Therefore, the metal permittivity should be negative in order to support surface waves. From Eq. (1.10) we know that it only works at frequencies smaller than the plasma frequency ω_p . This surface wave represents the combined excitation of free space electromagnetic wave and collective oscillation of electron gas in metal (Fig. 1.3(a)), and is named as surface plasmon polaritons (SPPs). The electromagnetic field decays exponentially away from the metal-dielectric interface as shown in Fig. 1.3(b). It is also obvious

from the analytical form in Eq. (1.30) ~ (1.35). Therefore, the largest field is achieved close to the interface. The field enhancement compared with incident wave can easily reach several fold and higher. The stronger absorption induced by larger local field has applications in various fields, e.g. plasmon enhanced solar cell[3]-[5], plasmon enhanced upconversion luminescence[6]-[8], and heat-assistant magnetic recording[9]. I will discuss the first two applications in more details later in this thesis.

1.3.2 Dispersion relation

As discussed from last section, the surface plasmon polaritons combine the character of free space electromagnetic wave and electron oscillations. It is expected that the dispersion relation should deviate from the light line: $\omega = ck$. The surface plasmon wave number β fulfills the equations

$$k_1^2 = \beta^2 - k_0^2 \epsilon_d \quad (1.38)$$

$$k_2^2 = \beta^2 - k_0^2 \epsilon_m \quad (1.39)$$

Combining with the Eq. (1.37), the surface plasmon wave number is

$$\beta = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (1.40)$$

Substituting $k_0 = \omega/c_0$ into β yields the dispersion relation of surface plasmon

$$\omega = \sqrt{\frac{\epsilon_m + \epsilon_d}{\epsilon_m \epsilon_d}} c_0 \beta \quad (1.41)$$

For comparison, we re-write the dispersion relation of electromagnetic wave in dielectric

$$\omega = c_0 k / \sqrt{\epsilon_d} \quad (1.42)$$

Eq. (1.42) is also known as “light line”. It is important to note from Eq. (1.37) that the dielectric function of metal ϵ_m has the opposite sign of ϵ_d to support SPPs. Therefore, for a certain frequency range, the SPPs has larger wave number β than the free space case. In other words, the wavelength of SPPs can be much shorter than free space light wavelength. This allows applications of SPPs in super resolution imaging[10]-[12] and sub-wavelength optical tweezers[13].

To better understand the dispersion relation, I plot the dispersion curve of SPPs at the interface of gold and fused silica in Fig. 1.4. The Drude model is used for gold dielectric function (Eq. (1.9)) with $\omega_p = 1.35 \times 10^{16} \text{ s}^{-1}$, $\Gamma = 1.08 \times 10^{14} \text{ s}^{-1}$. And $\epsilon_d = 2.25$ is used for fused silica. At low frequencies, the SPPs dispersion is close to the light line (black curve in Fig. 1.4). As the frequency is increased, the dispersion of SPPs deviates from the light line, lying to the right side. In this region, the wave number of SPPs is larger than that of the free space electromagnetic wave. Near the half of the plasma frequency, the SPPs wave number β reaches its maximum which corresponds to the smallest wavelength and group velocity. In the limit of negligible damping, the wave number can reach infinity, where the corresponding frequency is known as surface plasmon frequency ω_{sp} , and the mode is known as surface plasmon. The surface plasmon frequency ω_{sp} can be calculated from Eq. (1.40) and Drude dielectric model Eq. (1.10) for metal at visible frequency. I re-write them here.

$$\epsilon_m + \epsilon_d = 0 \quad (1.43)$$

$$\epsilon_d(\omega_{sp}) = 1 - \frac{\omega_p^2}{\omega_{sp}^2} \quad (1.44)$$

For air $\epsilon_d = 1$, the surface plasmon frequency ω_{sp} equals to $\omega_p / \sqrt{2}$. Similarly, for fused silica, the surface plasmon frequency ω_{sp} equals to $\omega_p / 1.8$ as shown in Fig. 1.4. Up to the surface plasmon frequency ω_{sp} , the SPPs is bounded to the metal-dielectric interface, which is the bounded mode.

With further increased frequency, the real part of the SPPs wavelength decrease to close to zero, and the imaginary part dominates. It prohibits propagation of surface plasmon polaritons. For frequency higher than the plasma frequency ω_p , the dispersion curve of SPPs lies on the left of light line that the wave number is smaller than the corresponding free space wave number. The SPPs radiates out as radiative modes.

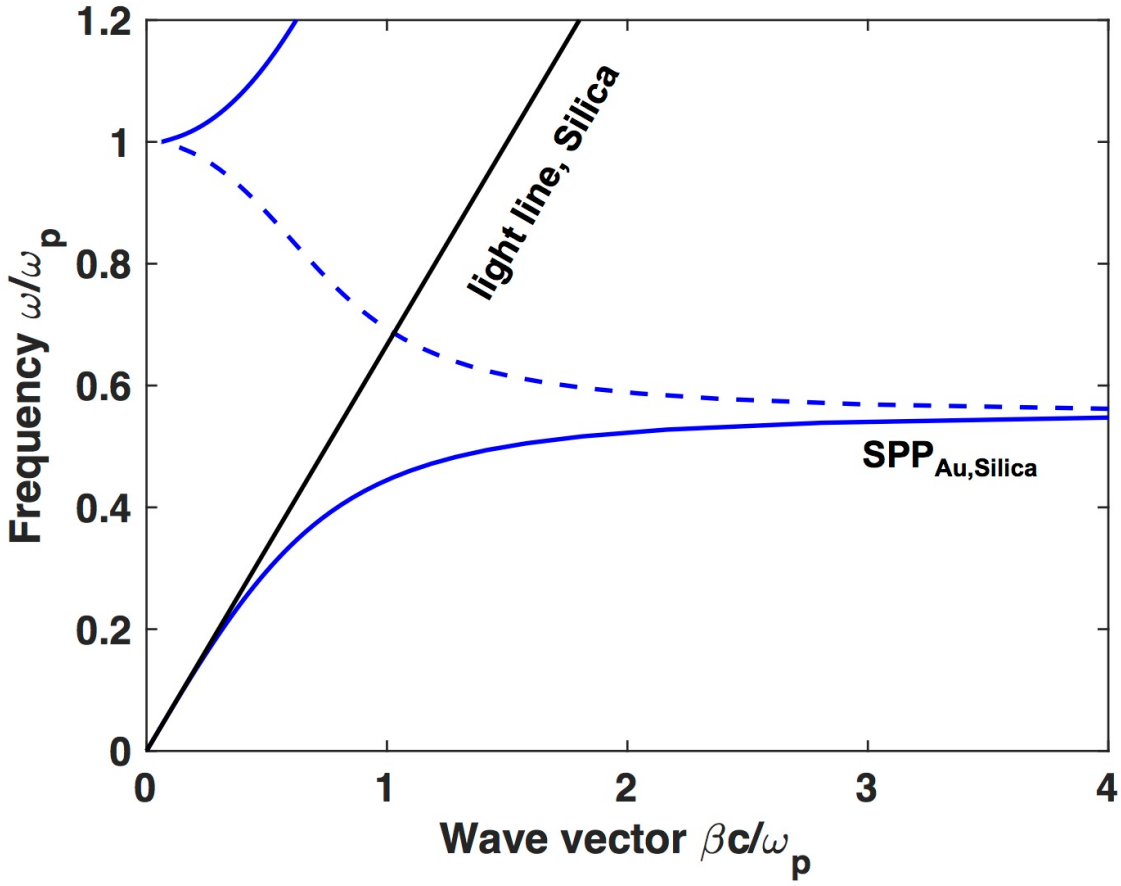


Figure 1.4 Dispersion relation of SPPs at the interface of gold and fused silica (solid blue curve for real part, dashed blue curve for imaginary part). The light line in fused silica is represented in black line. The frequency (y-axis) is normalized to plasma frequency ω_p , and the wave number (x-axis) is normalized to c/ω_p .

1.3.3 Local density of electromagnetic states

In optics, the local density of electromagnetic states (LDOS) refers to the number of states that can be occupied by a photon at the frequency ω . It is a critical parameter in characterizing lots of optical properties, e.g. electromagnetic energy density and spontaneous transition rates.

In the free space, the LDOS is known to be

$$\rho_v = \frac{\omega^2}{\pi^2 c^3} = \frac{n^3 \omega^2}{\pi^2 c_0^3} \quad (1.45)$$

It is proportional to the square of angular frequency, and to the cubic power of refractive index n . The LDOS is commonly defined as being the imaginary part of the trace of the electric field Green dyadic. However, according to J. J. Greffet *et. al*[14], the LDOS should also include the contribution from magnetic field with a more rigorous definition

$$\rho(\mathbf{r}, \omega) = \frac{\omega}{\pi c^2} \text{Im} \text{Tr} \left[\overleftrightarrow{\mathbf{G}}^E(\mathbf{r}, \mathbf{r}, \omega) + \overleftrightarrow{\mathbf{G}}^H(\mathbf{r}, \mathbf{r}, \omega) \right] \quad (1.46)$$

Here, the $\overleftrightarrow{\mathbf{G}}^E$ and $\overleftrightarrow{\mathbf{G}}^H$ are the dyadic Green function at angular frequency ω in spatial position $\mathbf{r}$ of electric and magnetic field, respectively. The Tr is the trace operator, and Im is the operator for imaginary part of a complex number.

The analytical solution of LDOS is available for limited cases of high symmetric geometries. The planar metal-dielectric interface for SPPs is one of them. The total LDOS is given as:

$$\begin{aligned} \rho(z, \omega) = & \frac{\rho_v(\omega)}{2} \left\{ \int_0^1 \frac{\kappa d\kappa}{q} \left\{ 2 + \kappa^2 \left[\text{Re} \left(r_{12}^s e^{i2q\omega z/c} + r_{12}^p e^{i2q\omega z/c} \right) \right] \right\} \right. \\ & \left. + \int_1^\infty \frac{\kappa^3 d\kappa}{|q|} \left[\text{Im} \left(r_{12}^s + r_{12}^p \right) e^{-2|q|\omega z/c} \right] \right\} \end{aligned} \quad (1.47)$$

Here, κ is wave number in unit of ω/c_0 . $q = \sqrt{1 - \kappa^2}$, z is the distance away from the interface,

ρ_v is the free space LDOS expressed in Eq. (1.45). r_{12}^s and r_{12}^p are the Fresnel reflection coefficients between media 1 and 2 in s and p polarizations, respectively, for a parallel wave number $k_{//} = \kappa \omega / c_0$. They are given as:

$$\begin{aligned}
r_{12}^s &= \frac{k_{1z} - k_{2z}}{k_{1z} + k_{2z}} \\
r_{12}^p &= \frac{\epsilon_2 k_{1z} - \epsilon_1 k_{2z}}{\epsilon_2 k_{1z} + \epsilon_1 k_{2z}}
\end{aligned}
\tag{1.48}$$

where $k_{iz} = \sqrt{k_i^2 - k_{//}^2}$ is the perpendicular wave number. It is clear from Eq. (1.47) that the LDOS expression is actually a summation of contributions from propagating waves (1st term) and evanescent waves (2nd term).

The material properties are embedded into the Fresnel reflection coefficients. Taking the gold-air interface for example, the LDOS is calculated from Eq. (1.47) over frequency from 1×10^{14} rad/s to 1×10^{17} rad/s at different z distances away from the gold surface as shown in Fig. 1.5. For the gold dielectric function, I used the Drude model with plasma frequency ω_p and damping coefficient Γ stated in the previous sections.

At distance 1 μm away from gold-air interface, the influence from gold is so weak that the LDOS equals to the free space vacuum LDOS which is contributed all from propagating modes. As the distance is reduced, the LDOS deviates more significantly from vacuum LDOS and the additional contribution from evanescent mode significantly increases the total LDOS. At 1 nm distance, the LDOS can be 6 orders larger than the vacuum LDOS. The LDOS has a resonant peak located at around 1×10^{16} rad/s in this case. Recall the surface plasmon frequency from the last section, $\omega_{sp} = \omega_p / \sqrt{2} = 9.6 \times 10^{15}$ rad/s. At the surface plasmon frequency, the dispersion curve flattens out as shown in Fig. 1.4 which indicates a large number of states available for photon occupation for a given frequency. Therefore, the LDOS peak is due to the surface plasmon resonance of gold. A similar peak of LDOS is also observed for SiC surface supporting surface phonon polaritons[15]. It is also interesting to note that at frequencies slightly

above the ω_{sp} the LDOS is smaller than the free space LDOS (see, for example, $z = 10$ nm case in Fig. 1.5), though the LDOS remains much larger than the free space LDOS over the majority of the frequencies.

The LDOS is important in characterizing the electromagnetic energy density, $U(\mathbf{r}, \omega)$,

$$U(\mathbf{r}, \omega) = \rho(\mathbf{r}, \omega) \frac{1}{\exp(\hbar\omega/k_B T) - 1} \hbar\omega \quad (1.49)$$

Here, k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant. The energy density is linearly proportional to LDOS. Large LDOS close to the gold-air interface indicates large amount of energy stored in the near field by evanescent waves, especially at the surface plasmon frequency. It attracts lots of interest in harvesting the energy stored in the near field[16], [17]. I will discuss it in more details in a later chapter. The LDOS is also of interest in controlling the photon emission, known as the Purcell effect[18]. The radiative emission rate is linearly proportional to the LDOS at the position of the quantum emitter. Various plasmonic structures[19]-[23] have been designed to engineer the LDOS, thus the emission rate. In addition, there is lots of research going on for the near field heat transfer[24]-[26] which also takes advantage of the increased LDOS by evanescent waves, although it is beyond the scope of this thesis.

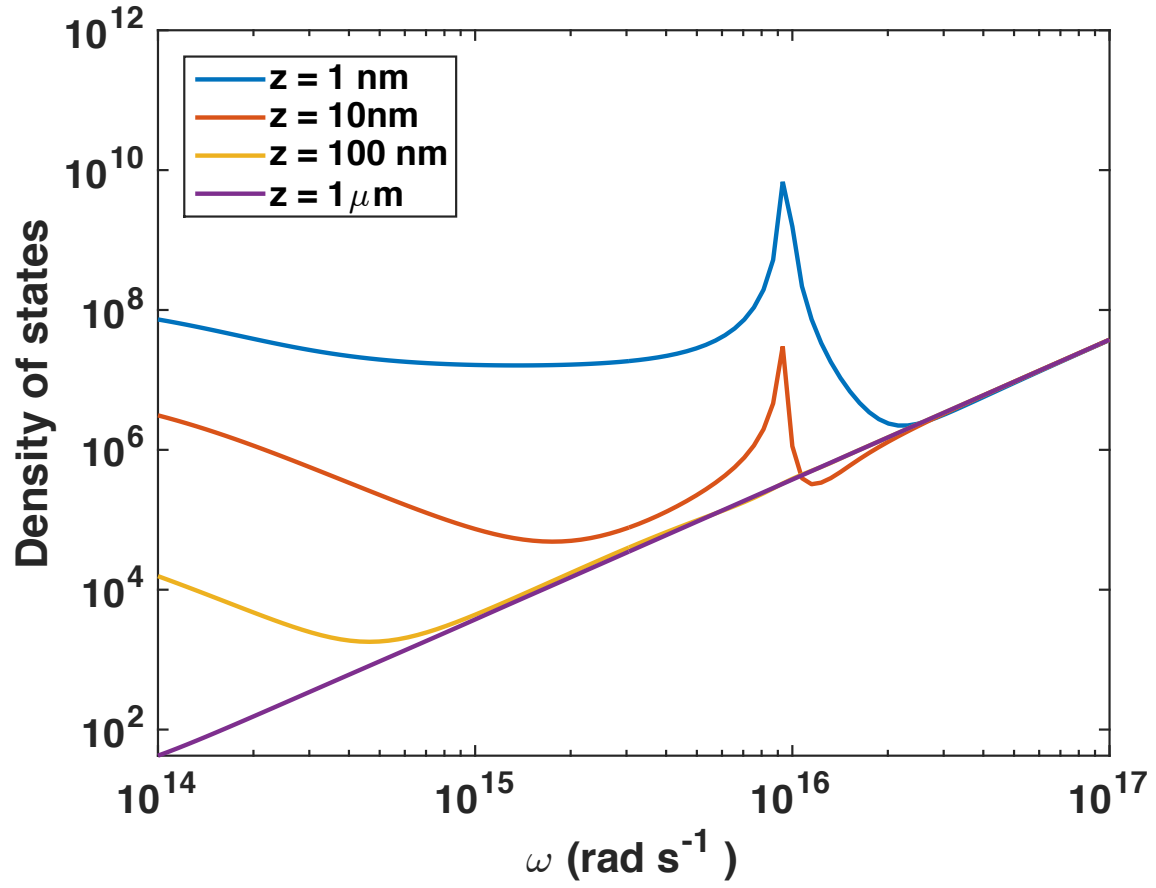


Figure 1.5 LDOS of planar gold-air interface with distance z away from the gold surface. Different color of the curves correspond to different distance as shown in the legend. Both axis are in logarithmic scale.

1.3.4 Excitation of surface plasmon polaritons

From the dispersion relation of SPPs we know that the wave number of SPPs is larger than the free space light at the same frequency, thus momentum matching is required to couple free space light into SPPs. In this section, I will discuss several popular configurations for SPPs excitation: Prism coupling (Kretschmann configuration[27], Otto configuration[28]), diffraction by periodic structure and small aperture, and scattering.

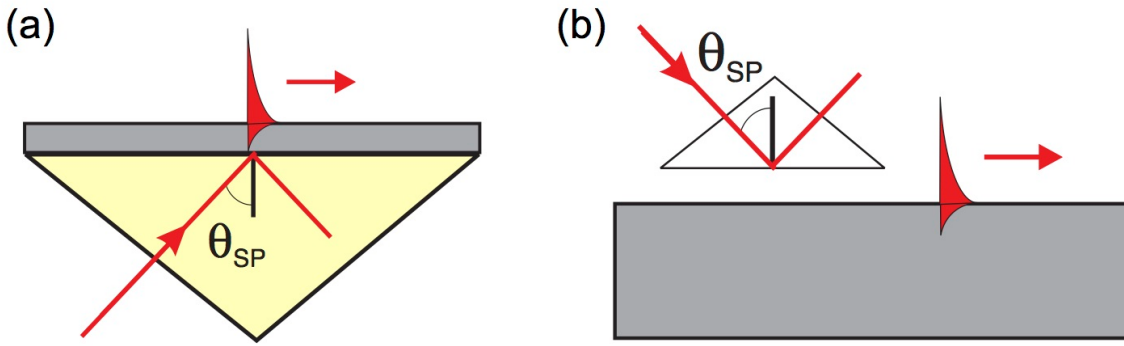


Figure 1.6 The Kretschmann configuration (a) and Otto configuration (b). Metal slab is in gray color. The triangle object is dielectric prism. They are put in air. The SPPs coupling angle is θ_{sp} . The incident TM polarized light is in red line marked with incident direction by arrow, and the coupled SPPs propagation direction is denoted by red arrow (ref [29]).

For convenience, I re-write the wave number of SPPs here

$$k_{sp} = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (1.50)$$

Again, k_0 is the free space wave number, ϵ_m and ϵ_d are the dielectric index of metal and dielectric, respectively. In prism coupling as shown in Fig. 1.6, the SPPs reside on the interface of metal and air, which corresponds to $\epsilon_d = 1$. Matching the horizontal wave vector component of the incident light to k_{sp} , yields the coupling angle θ_{sp}

$$k_{sp} = k_0 \sqrt{\epsilon_{prism}} \sin \theta_{sp} \quad (1.51)$$

Simple calculation can find that the coupling angle θ_{sp} is larger than the critical angle that the incident light has total internal reflection (TIR) at the prism-metal interface. The evanescent wave generated at the TIR tunnels through the thin gap (silver in Kretschmann configuration, air in Otto configuration) to couple into the SPPs. For efficient tunneling, the thickness of the silver or air gap should be thinner than the wavelength.

The incident light couples to SPPs only when the wave vector matches. At angle θ_{sp} , the coupling efficiency can be almost 100% which results in a resonant dip in reflection spectra (Fig. 1.7). The angle θ_{sp} is sensitive to environmental dielectric index as shown in Fig. 1.7, which spawns wide applications in gas detection and bio sensing[30]-[33].

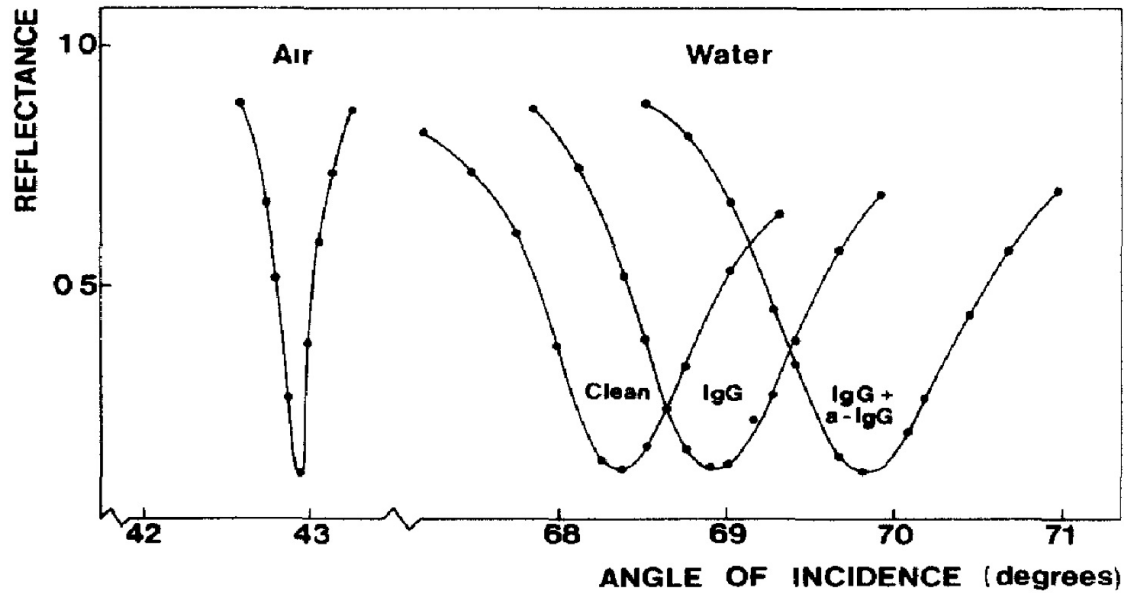


Figure 1.7 Reflection measured over different incident angles for Kretschmann configuration with thin silver film put in different environments: air, clean water, water with IgG, and water with a-IgG. (Ref. [30])

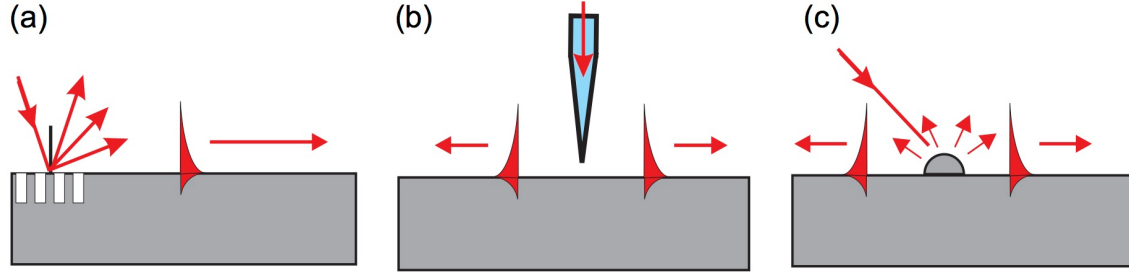


Figure 1.8 Coupling by diffraction and scattering. (a) Incident light diffracted by grating structure. (b) Incident light diffracted from subwavelength aperture couples. (c) Incident light scattered by small particle. The incident TM polarized light is in red line marked with incident direction by arrow, and the coupled SPPs propagation direction is denoted by red arrow. (Ref. [29])

TM polarized incident light can also couple into SPPs by periodic structures. As shown in Fig. 1.8(a), a grating can provide additional lateral wave vector $\Delta k = m \cdot 2\pi / \Lambda$ to the incident light, where m is the diffraction order and Λ is the periodicity. The frequency of SPPs depends on the angle of incident light, and the grating period. For incident angle θ_{in} and period Λ , the coupling condition is

$$k_{sp} = k_0 \sin \theta_{in} + m \frac{2\pi}{\Lambda} \quad (1.52)$$

where m is integer. It is important to note that the SPPs can propagate in both directions that the wave number k_{sp} can be positive and negative. At normal incidence, the opposite propagating SPPs are at the same frequency resulting in a single dip in the reflectance spectrum. One example of periodic nanograting coupled SPPs is given in Fig. 1.9. The silver nanograting has a period of 830 nm with grating height 20 nm and width 430 nm. The coupled surface plasmon resonance is located at around 850 nm. This is the nanograting I used for surface plasmon enhanced upconversion luminescence study[6]. I will discuss it in details in chapter 3. It is important to note that the silver nanograting alone has relatively shallow resonance thus smaller

surface plasmon coupling efficiency at around 850 nm as shown in Fig. 1.9. However, the whole sample, which includes nanograting, Si_3N_4 and upconversion nanoparticles, is designed to have almost 100% coupling efficacy targeting at 980 nm.

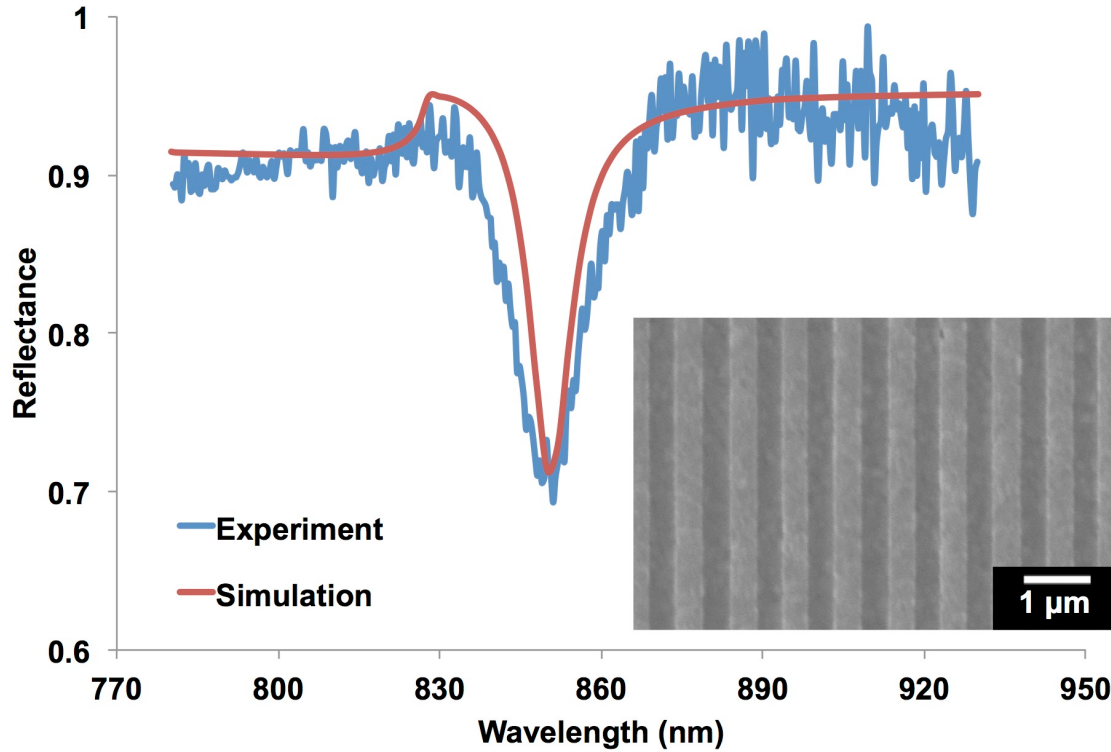


Figure 1.9 Reflectance spectrum of silver one-dimensional nanograting under normal incidence of white light from tungsten lamp. The experimental data and simulation results are shown in blue and red, respectively. The inset is the scanning electron micrograph of the nanograting. The 1 μm length scale is given by the white bar.

Other coupling configurations include subwavelength tip and nanoparticle scattering shown in Fig. 1.8 (b) and (c), respectively. The former relies on the diffraction by the subwavelength size tip so that some of the incident light gain large wave vector that matches the momentum of SPPs. The latter relies on the Mie scattering[34] by the nanoparticle that can produce waves matching the momentum of SPPs. Compared with other coupling techniques, the

efficiency of these two configurations are generally low. However, it allows the excitation of SPPs at specific positions with precise control.

1.4 Experimental setup

I conduct two major types of spectroscopy experiments to characterize the samples. One is the reflectance spectrum measurement mainly used in characterizing the quality of grating samples. With minor changes, the same setup can also measure the photoluminescence (PL) of upconversion nanoparticles (UCNPs). The other is the time-resolved PL spectroscopy measurement for transient upconverted luminescence.

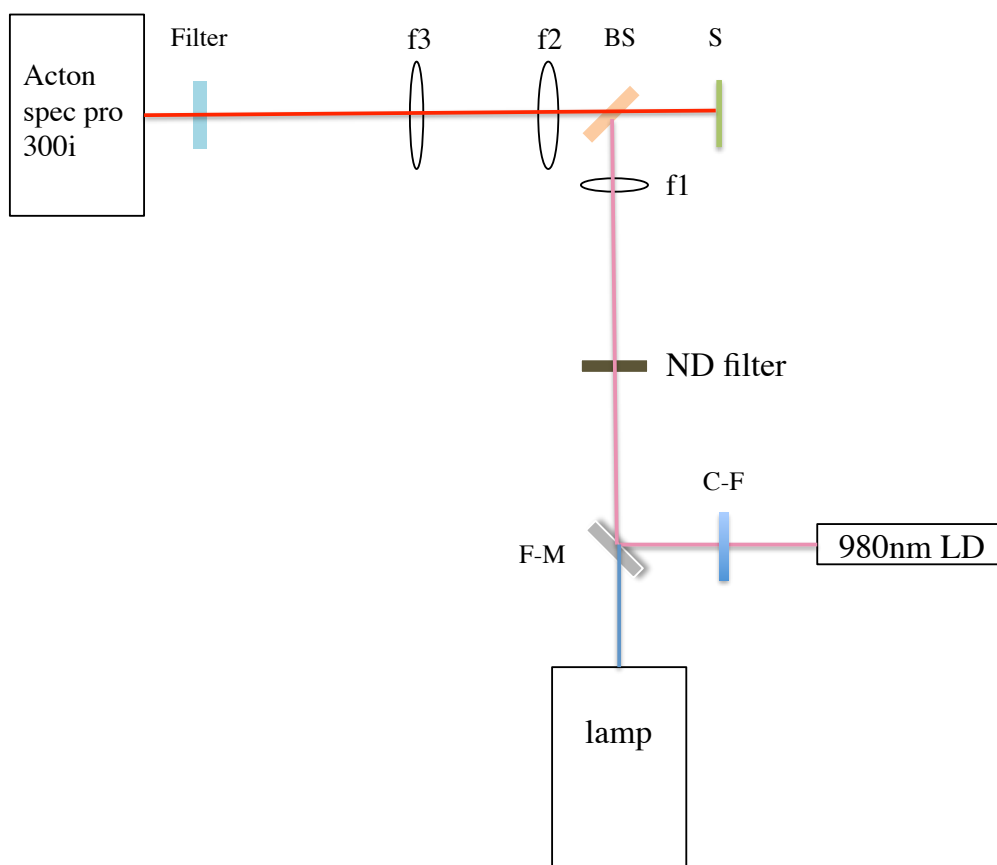


Figure 1.10 Experimental setup for reflectance spectrum measurement of grating sample, and photoluminescence measurement of upconversion nanoparticles. In the sketch, C-F represent the cleanup filter, F-M represents the flip mirror, ND filter represent the neutral density filter, BS represents the beam splitter, S represents the sample position, $f_1 \sim f_3$ represent convex lenses.

Let us start with the setup for reflectance measurement and PL measurement (Fig. 1.10). In the reflectance measurement, the flip mirror (F-M in Fig. 1.10) is pressed down so that the white light from tungsten lamp can pass through. The incident light is polarized in the direction orthogonal to grating lines to excite the surface plasmon modes. The incident light is focused by a convex lens (f1), and directed to the sample through a beam splitter cube at normal incidence. A collimating lens (f2) with focal length of 5 cm is used to collect reflected light from the sample. The collimated light is then refocused onto the spectrometer entrance slit with a numerical aperture matched focusing lens (f3). The reflectance spectrum of the grating sample is resolved by a grating spectrometer (Acton SpectraPro 300i) with liquid nitrogen cooled Si charge-coupled device (CCD) detector and thermoelectric cooled InGaAs CCD (Andor) detector to cover the wavelength range from visible to near infrared. The source spectrum was measured in exactly the same way but the sample replaced by a highly reflective mirror for calibration. Reflectance spectrum is obtained by dividing the reflection from the grating samples to the source spectrum.

The PL spectroscopy is conducted by the same collection optics and spectrometer as the reflectance spectroscopy. Take the visible PL spectroscopy measurement for example. The excitation source switches to a 980 nm laser diode (OEM laser) that coupled into the system by the flip mirror (F-M). A clean up filter (Semrock LL01#980) with bandwidth of 3.7 nm is used to remove laser tail outside central laser wavelength. A dichroic mirror, which replaced the beam splitter cube, directs the laser beam onto the sample at normal incidence while transmitting the visible PL signal from the UCNPs. The visible emission is focused onto spectrometer by the collection optics and detected by a liquid nitrogen cooled Si CCD detector. Similarly, the NIR

emission spectrum is measured with an NIR beam splitter and InGaAs CCD detector. In order to protect the detector from the excitation laser, a short-pass edge filter (Schott KG5) is placed right before the spectrometer entrance slit.

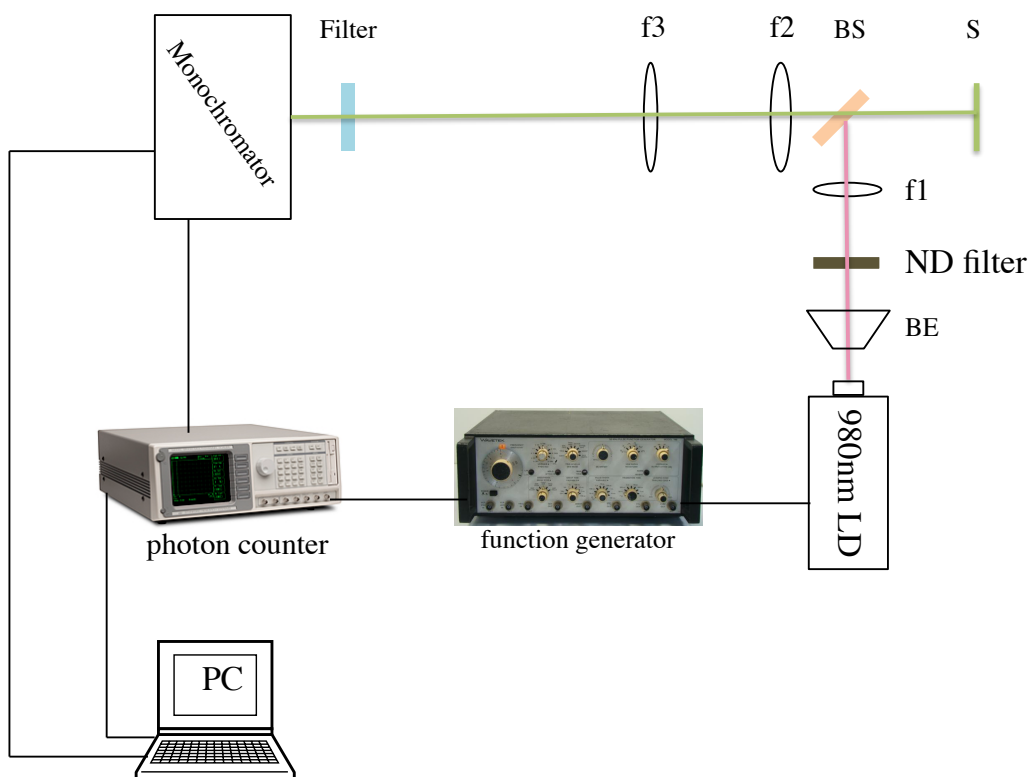


Figure 1.11 Time-resolved spectroscopy setup. BE represent the beam expander, ND filter represent neutral density filter, S represents the sample position, $f1 \sim f3$ represent the convex lenses. BS represents the beam splitter.

In the time-resolved PL spectroscopy (Fig. 1.11), a square pulse train of 980 nm light from laser diode (Thorlabs L980P200) is used to excite UCNPs at normal incidence. The laser pulse duration and duty cycle are controlled by a function generator (Wavetek model 166) connected to the laser diode current driver (Thorlabs TCLDM9). For the transient NIR PL

presented in chapter three, I used a square wave with 20 ms period and 50% duty cycle. A band-pass filter (Semrock LL01-980) with 3.7 nm bandwidth centered at 980 nm is placed in front of the laser to filter out side band emissions. Then, the cleaned laser beam is expanded by a 5x achromatic Galilean beam expander to the diameter around 1 cm before it is focused tightly onto the sample surface by a convex lens (f_1). One neutral density filter is used to attenuate the excitation laser to different powers. The excitation laser beam is directed onto the sample at normal incidence using a NIR beam splitter cube. For the plasmonic nanograting sample, I align the laser polarization orthogonal to the nanograting lines. The emission from the UCNPs is collimated and re-focused to a monochromator (Sciencetech 9057F) by two convex lenses (f_2 and f_3). For transient NIR PL detection, I place one long-pass filter (Semrock BLP01-980R) before the monochromator entrance slit to attenuate the laser light and pass only the NIR emission from UCNPs. The monochromator is set at 1002 nm, and the transient PL signal is recorded by a NIR photomultiplier tube (Hamamatsu H10330B-75), which is connected to a photon counter (Stanford Research Systems SR430). The photon counter input is synchronized with the laser pulse by the function generator, and the transient NIR PL is stored in the internal memory of photon counter.

The same setup is also used for the transient green PL detection with the same 980 nm laser pulse excitation except that I replace the long-pass filter (Semrock BLP01-980R) by short-pass edge filters (Scott KG5), and deliver 550 nm light to a visible PMT (Hamamatsu H11461P-11). I also measured the transient green PL under green laser (Thorlabs, DJ532-40) excitation at 532 nm using the same setup. The side band of excitation green laser is filtered by band-pass filter (Semrock FF01-524/24). Before the monochromator entrance, the excitation green laser is

attenuated by long-pass filter (BLP01-532R-25). For the green laser pulses, the square waveform has a period of 40 ms with 50% duty cycle.

1.5 Dissertation outline

This thesis studies the applications of plasmonics in energy harvesting, including solar energy conversion and near field thermal energy harvesting.

Chapter two focuses on the application of plasmonics in organic photovoltaics (OPV). The efficiency of OPV, and other types of semiconductor photovoltaics, is limited by the inability of absorbing photons with energy below the bandgap. By designing plasmonic nanograting with resonance at the absorption edge, ~10% overall absorption improvement is achieved. Both localized and propagating surface plasmon modes are observed in the device. Their interaction, and the influence on overall absorption are studied in details.

Chapter three will continue the study of improving photovoltaic efficiency from a different perspective. Instead of expanding the absorption band of the photovoltaics, this chapter will focus on the engineering of the solar spectrum by converting the long wavelength photons into well-absorbed visible photons through an upconversion material. In order to improve the upconversion PL and the efficiency, surface plasmon is introduced to the upconversion system. By tuning the surface plasmon resonance to the upconversion frequency with silver nanograting structure, I improve the PL of upconversion material by 39-fold maximum. The rate equation analysis of both the steady state and transient PL reveals that the efficiency improvement is achieved by roughly 3-fold absorption enhancement and 2-fold energy transfer enhancement with plasmonics.

In chapter four, I will switch the focus from solar energy to near field thermal energy. I designed metamaterial to excite the spoof surface plasmon in the terahertz frequency for strongly enhanced thermal emission. The FDTD simulation developed from the fluctuation electrodynamics demonstrates several hundredfold enhancement of thermally excited

electromagnetic energy in the near field. It opens the avenue for efficient thermal energy harvesting in the near field.

The last chapter will summarize the thesis. Future work and outlook are presented in each chapter separately.

2 Surface plasmon enhanced organic photovoltaic device

2.1 Introduction

The photovoltaic (PV) technology moves on to the next-generation devices which typically incorporate thin film active layers as opposed to the bulk silicon technology that has dominated the market for decades. Compared with the traditional semiconductor solar cell, the organic photovoltaic (OPV) device made of conjugated organic polymer has many advantages[35]. First, the OPV material can be produced by solution phase techniques, e.g. ink jet printing or roll-to-roll technique, which could potentially lead to high throughput, cheap manufacturing. Thanks to the mechanical flexibility of organic polymer and the light-weight, the OPV has the potential to integrate with flexible electronics into wearable devices[36], [37]. However, the wide-spreading applications of OPV devices are currently bottlenecked by its relatively low efficiency, which is reported around 10% as the highest. Limited by the short exciton diffusion length in conjugated polymers[38], [39], the active layer of OPV is usually thin. As the active layer thickness becomes comparable to or small than the absorption length, the device cannot absorb all incident light and thus light management techniques that can enhance absorption become important. There is vast literature on absorption enhancement using various structures among which plasmonic nanostructure is of particular interest thanks to the strong local field enhancement plasmon resonances naturally provide. Surface plasmon effect can improve PV device performance in several different ways: (1) enhanced scattering of incident light into high index active layer, (2) enhanced absorption due to local field enhancement, and (3) light in-coupling via diffraction grating[4]. Enhanced light in-coupling due to scattering is more relevant to

inorganic semiconductor based PV devices in which high index semiconductor layers typically exhibit high Fresnel reflection. For OPV devices, a combination of (2) and (3) is more effective.

Various attempts have been made to incorporate plasmonic nanostructures in OPV devices. They include embedding plasmonic nanoparticles inside the active layers[40], [41], and 1D or 2D grating structures on either the front[42]-[44], back[3], [45], [46] or both surfaces[47], or a combination of both nanoparticles and grating[48]. Among these, designing a plasmonic grating structure that could be patterned on the back-electrode is especially attractive as it requires minimal modifications on the conventional device structure. Several groups have investigated organic solar cells with 1D/2D grating on back-electrodes and reported absorption enhancement ranging from 13% to 83%[3], [45], [46], which depended on the active layer thickness and other details of the structure. Missing in the literature is the possible presence of multiple modes which may interact with one another. For example, it has been shown that a localized plasmon mode can interact strongly with waveguide modes in a dielectric layer with metallic grating[49]. When the OPV with patterned back-electrode supports multiple modes, such an interaction should affect the absorption properties.

In this chapter, I will first introduce the design of patterned back-electrode, which can support the surface plasmon modes in OPV device. Thanks to the enhanced local field from the surface plasmon mode, the absorption of the OPV device is enhanced by around 10%. More detailed study reveals two plasmonic modes in the device: surface plasmon polaritons (SPPs) and localized surface plasmon polaritons (LSPPs). The two modes exhibit strong interaction as indicated by anti-crossing behavior. And I will discuss the influence of the absorption properties from the mode interactions. Later, I have experimentally investigated the surface plasmon effects

on the fabricated sample based on our back-electrode design. The experimental results validate the modeling analysis.

2.2 Patterned back-electrode design for plasmon enhanced OPV device

In this study, I investigate the effect of plasmonic grating structures fabricated on the back-electrode of an OPV layer made of a blend (1:2 by weight) of poly[N-900-hepta-decanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole)] (PCDTBT) and phenyl-C61-butyric-acid-methyl-ester (PCBM). PCDTBT is one popular semiconducting polymer[50] with which high performance OPV devices have recently been reported[39], [51]. Similar to many other OPV materials, PCDTBT has an absorption edge near 660 nm. And one of the challenges is to expand the absorption band further into the red and near-infrared region. A simple grating structure can be incorporated on the back-electrode to enhance absorption near the band edge. I performed the finite-element modeling using commercial software (COMSOL Multiphysics) to design a suitable grating pattern on the silver back-electrode. Here, the discussion is focused on transverse magnetic (TM, E-field perpendicular to grating alignment) polarization because the 1D grating structure exhibits plasmon resonances for TM polarization only. Transverse electric (TE, E-field parallel to grating lines) polarization shows almost identical absorptance spectrum except for the absence of the surface plasmon modes. This polarization dependence can be eliminated by designing a two-dimensional structure but one-dimensional grating under TM polarization offers an adequate model system to study the plasmon mode behaviors. The simulation shows that one of the effective designs is a grating with period of 500 nm with grating line width of 220 nm and thickness of 20 nm, as schematically shown in the inset of Fig. 2.1(a).

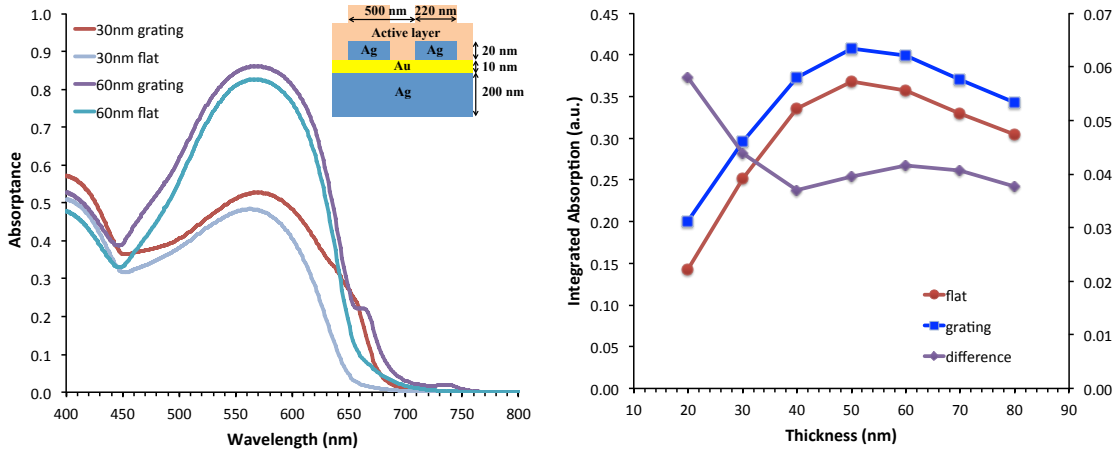


Figure 2.1 (a) Absorption by the PCDTBT:PCBM layer under TM polarization excitation on flat silver film and the grating structure. The inset shows the schematic of the grating structures with dimensions. The results from different structures are in different colors denoted in the legend. (b) Total absorption integrated over the visible to near-infrared region under TM polarization excitation for various thicknesses of PCDTBT:PCBM layer. The difference in total absorption between flat silver film and grating is also plotted on the secondary axis (on the right side).

I first conducted an extensive numerical modeling study. In this study, experimentally measured dielectric functions for PCDTBT:PCBM, silver and gold were used[51], [52]. In order to separate the absorption by metal from that by the active layer, I used the standard technique of integrating the electromagnetic energy within the active layer volume to estimate the power dissipated within the active layer only[53]. The absorption by the 30 nm and 60 nm thick PCDTBT:PCBM layers on flat silver film and grating structure are shown in Fig. 2.1(a). The absorption is increased at all wavelengths when grating structure is introduced but particularly so at wavelengths 650 nm and longer. An interesting observation is that the 60 nm PCDTBT:PCBM on grating exhibits two peaks, while the 30 nm thick sample shows only one peak. To search for the origin of these absorption peaks, I conducted numerical simulations for various thicknesses between 20 nm and 80 nm. Before I get into the details of the different plasmon modes, I first

assessed the effect of grating on overall absorption across the entire absorption band by integrating the absorptance spectrum over the visible and near-infrared region where PCDTBT:PCBM has non-negligible absorption. The integrated absorption plotted in Fig. 2.1(b) represents the fraction of power absorbed by PCDTBT:PCBM when the incident radiation has uniform power spectrum. The total absorption reaches a maximum when the thickness is 50 nm and decreases for larger thicknesses despite the larger volume of absorbing material. This behavior is attributed to the interference between the incoming and reflected light in much the same way as typically observed in an anti-reflection coating[47]. Comparing the same thickness active layers with and without the grating structure, the ones with backside grating has higher absorption in all cases. The absorption enhancement is highest for 20 nm case and decreases down to 11~12% range for larger thicknesses under TM polarization. For TE polarization, surface plasmon modes is not excited and the absorption spectrum remains almost the same as the flat case. If we take the average of the two polarizations, the enhancement is 10.2% for the 30 nm case and 8.6% for the 60 nm case. The absorption enhancement factor decreasing with increasing active layer thickness is commonly observed. A thinner layer absorbs less and thus offers larger room for enhancement while a thicker layer absorbs more light to begin with and thus tends to show smaller enhancement. However, Fig. 2.1(b) shows that enhancement begins to flatten at 40 nm and actually increases, albeit only slightly, to a maximum value at 60 nm thickness. This unusual behavior is actually related to the two absorption peaks observed for 60 nm sample in Fig. 2.1(a).

2.3 Mode interaction and its impact on OPV absorption

A closer examination of the absorption spectra of PCDTBT:PCBM on grating shows that there actually exist two peaks in all thicknesses. Some peaks couldn't be seen because they were buried inside the intrinsic absorption band of PCDTBT. To circumvent this difficulty, I repeat the same simulations after setting equal to zero the imaginary part of permittivity of PCDTBT:PCBM layer. This eliminates the intrinsic absorption band of PCDTBT while preserving the peak positions of absorption bands due to plasmon modes. The peak wavelengths of the two absorption peaks obtained this way are plotted for various active layer thicknesses in Fig. 2.2(a) in blue and red dots. Again, the peaks exhibit red shift with increasing active layer thickness resulting in larger effective index. However, the two peaks have very different slopes and show anti-crossing near the thickness of 30 nm. The peak exhibiting large shift with thickness corresponds to the coupling into the surface plasmon polaritons mode via grating coupling. To verify this, I numerically calculate the effective index of the SPPs mode in the 3-layer system consisting of thick metal substrate, thin dielectric PCDTBT:PCBM film and air for various dielectric layer thicknesses. Once the effective index of the SPPs modes is found, it is straightforward to calculate the wavelength that satisfies the grating coupling condition. The grating coupling wavelengths calculated this way are plotted in Fig. 2.2(a) in blue dashed line with crosses. As shown, the grating coupling wavelengths agrees well with the long wavelength absorption peaks for thicknesses of 40 nm or larger and also with the short wavelength peak at 20 nm thickness. It is thus confirmed that this branch corresponds to the grating coupling into the SPPs modes.

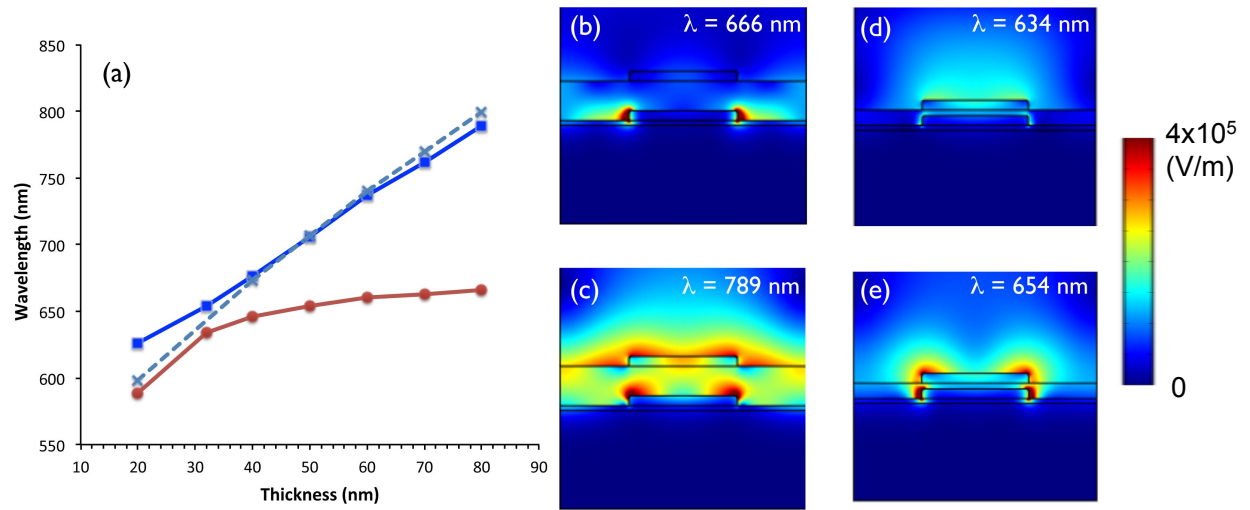


Figure 2.2 (a) Surface plasmon peak positions as a function of PCDTBT:PCBM active layer thickness exhibiting anti-crossing behavior. Blue and red solid dots represent LSPs and SPPs peak positions for various PCDTBT:PCBM thicknesses. Blue crosses represent the SPPs peak positions calculated from the effective index of the SPPs mode supported by the flat silver-PCDTBT:PCBM-air multilayer structure. (b,c) Electric field profiles for the surface plasmon modes in the 80 nm thick PCDTBT:PCBM on silver grating and (d,e) electric field profile for the surface plasmon modes in the 30 nm thick PCDTBT:PCBM on silver grating. The excitation power used here in simulation is 1 watt over unit cell size by 1 meter.

The other branch joining the shorter wavelength peaks at thicknesses over 40 nm with the longer wavelength peak of 20 nm thickness shows little changes with increasing active layer thickness. Furthermore, these peaks are also found to be largely insensitive to the grating period and incident angle as shown in Fig. 2.3. For these reasons, it is assigned to be LSPs mode. The nature of these modes are apparent in the field profiles shown in Fig. 2.2(b)-(e) with electric field amplitude at wavelengths of 666 nm and 789 nm, respectively, for the dielectric layer thickness of 80 nm. The LSPs mode at 666 nm has the field tightly confined on the sides of the grating line while the mode at 789 nm exhibits much more spread-out profile of the electric field than the LSPs mode. In terms of absorption enhancement, the SPPs mode generally shows larger

enhancement thanks to the favorable field profile where the field is more stretched out into the absorbing material. The numerical simulation shows the peak absorption enhancement estimated by the integrated energy density inside the 80 nm thick active material is 9.6x for SPPs mode compared with the flat film while it is 3.2x for LSPPs. When the two modes mix and exhibit anti-crossing, the field profile changes significantly as shown in Fig. 2(d) and (e). As a result of the mixing, the absorption enhancement due to these mixed modes is larger than the LSPPs mode but smaller than the SPPs mode. In the absorption spectra for the 30 nm sample in Fig. 2.1(a), the two mixed modes are not resolved due to the close proximity and were observed as a single shoulder feature extending the absorption edge. As the active layer thickness is further increased, the SPPs and LSPPs modes become well separated. Therefore, for the larger thickness samples, the LSPPs mode extends the absorption edge while the SPPs mode produced a new absorption band in the below-bandgap region. The combined contributions by the LSPPs and SPPs modes result in the slight increment in the absorption enhancement factor at thicknesses of over 50 nm shown in Fig. 2.1(b). This result shows the need to full understand the presence and interplay between the two different types of plasmon modes to fully optimize the plasmonic grating structure for OPV devices. It is noted that a real OPV device contains additional dielectric layers such as carrier blocking layers and transparent electrode. The presence of additional dielectric layers results in shift of surface plasmon polaritons wavelengths but the absorption enhancement remained mostly unchanged. For a structure consisting of 40 nm ZnO, 120 nm indium tin oxide (ITO) and optically thick glass on top of 80 nm thick active layer, the peak absorption enhancement was found to be 9.4x for SPPs mode and 3.4x for LSPPs mode, respectively.

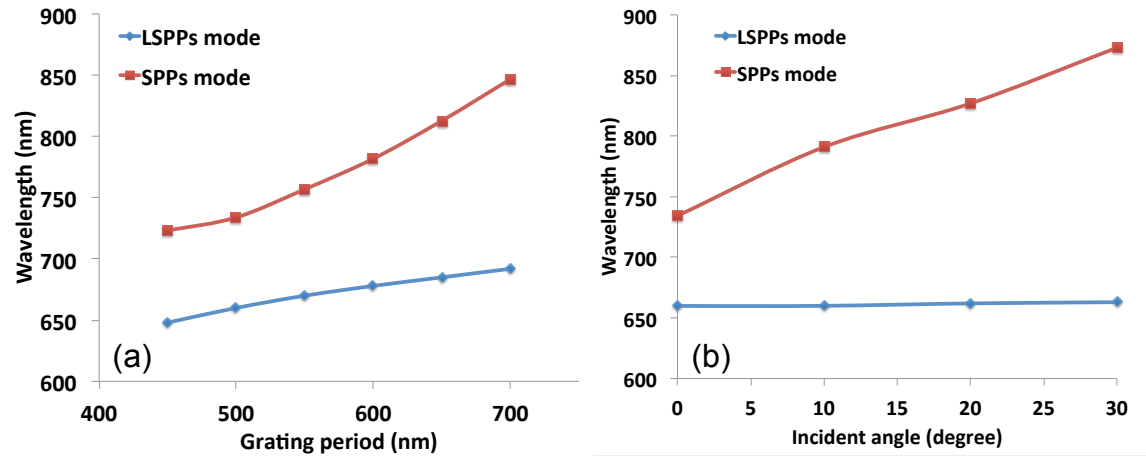


Figure 2.3 (a) The peak positions of LSPs mode and SPPs mode for different grating periods under normal incidence. (b) The peak positions of LSPs mode and SPPs mode for different incident angles with 500 nm grating period. The active layer thickness is 60 nm for both cases.

2.4 Experimental demonstration

To experimentally investigate the surface plasmon effects, we fabricated the grating structure by nano-imprint lithography. Briefly, a 200 nm thick silver film was deposited on a plastic substrate. Then, a 170 nm thick poly(methyl methacrylate) (PMMA) was spin-coated and the grating pattern was imprinted using a silicon mold. Any residual PMMA within the trenches was removed by a carefully controlled oxygen reactive ion etching (RIE). To prevent any oxidation of silver during the RIE process, 10 nm thick gold layer was deposited on top of silver before PMMA spin-coating. After imprinting, the PMMA pattern was transferred to silver grating pattern by evaporation of a 20 nm thick silver film and lift-off. As shown in the scanning electron micrograph in Fig. 2.4(a), a highly uniform nano-grating structure was obtained over a large area (0.64 cm²).

To characterize the gratings, reflectance spectrum was taken for normal incidence. The sample was illuminated at normal incidence by TM polarized broadband light from a tungsten lamp. The reflected light was collected by a pair of lenses and focused onto a spectrometer (Acton SpectraPro 300i) with liquid nitrogen cooled silicon detector. Since there is no transmission due to the thick silver backplane, the measured reflectance spectrum is easily converted to the absorptance spectrum, $A = 1 - R$. As shown in Fig. 4(b), the grating exhibits a well-defined absorption peak due to the grating coupling into the surface plasmon mode. The peak position and linewidth are in excellent agreement with simulations, attesting for the high quality of the fabricated structure. Once the good quality grating structures were obtained, PCDTBT:PCBM layers with various thicknesses were spin-coated. In Fig. 2.4(b), I also show absorptance spectra taken from 30 nm and 60 nm thick PCDTBT:PCBM layers deposited on flat silver films and on gratings. In both cases, PCDTBT:PCBM film deposited on grating shows

higher absorption at all wavelengths. The increased absorption over the broad range of the visible spectrum is attributed to the higher light scattering due to the surface corrugation induced by the back-electrode grating structure. In addition, both samples show additional absorption band below the absorption edge, which are due to the grating coupling into the surface plasmon modes. The 60 nm thick film exhibits the grating peak at a longer wavelength than the 30 nm thick film. This is naturally expected because a thicker film increases the effective index of the dielectric cladding and thus causes red shift of plasmon resonance[54]. Fig. 2.4(b) also shows simulated absorptance spectra fitting for grating and PCDTBT:PCBM layers on grating. In nanostructures, metals are known to exhibit higher loss due to increased scattering of free electrons by the surface and grain boundaries[55]. To account for this, I increased the imaginary part of the metal permittivity from the values given in Ref. [56]. The good agreement between the fitting and experimental spectra indicates that the increased imaginary permittivity values used in the fitting represented the real structures well. The increased metal loss naturally decreases the absorption by the active layer. While much of the absorption is due to metal, the active layer absorption is nonetheless increased too. From the absorptance spectra of 60 nm thick PCDTBT:PCBM on grating shown in Fig. 2.4(b), I extract the active layer absorption enhancement of 1.9x at the SPP mode wavelength. While the enhancement was decreased substantially from that obtained using the bulk dielectric function given in Ref. 20, it is still comparable to other techniques. For example, a dielectric grating patterned on ITO showed a peak absorption enhancement of $\sim 3x$ [57]. Considering that fabrication imperfections often deteriorate the performance of photonic crystals, the peak enhancement in real devices is expected to be about the same as our case.

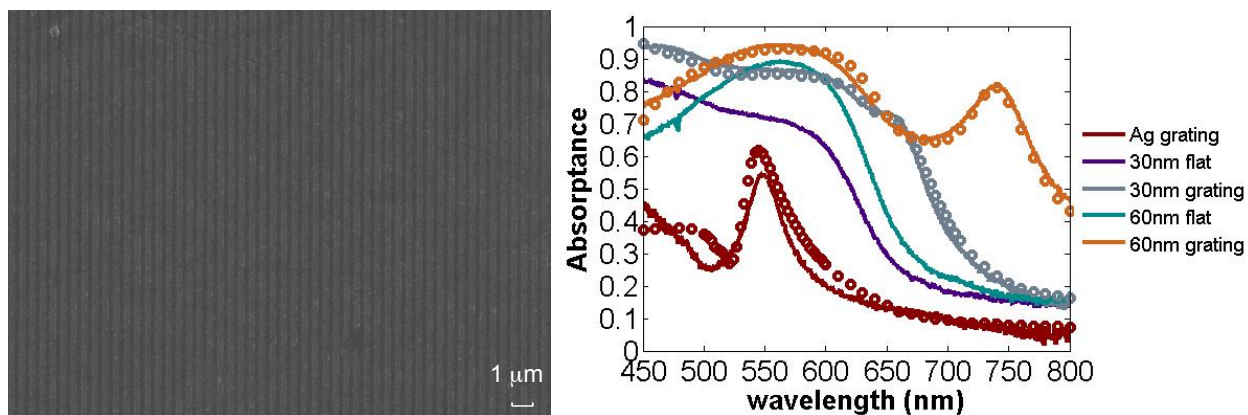


Figure 2.4 (a) Scanning electron micrograph of the silver nano-grating structure (scale bar indicates 1 μm). (b) Experimental absorbance (TM polarization) spectra for grating only (red), 30 nm thick PCDTBT:PCBM layer on flat silver film (purple) and on grating (grey), 60 nm thick PCDTBT:PCBM layer on flat silver film (light green) and on grating (orange). Symbols are simulations obtained using the exact structure parameters extracted from SEM and thickness measurements.

2.5 Summary

In summary, I investigate the effect of metal grating fabricated on the back-electrode of PCDTBT:PCBM OPV structure. Nanograting patterned back-electrode offers an effective way to incorporate plasmonic structures for photon management that requires minimal disturbances to the device structure. It shows that the introduction of back-electrode grating increased absorption by the active layer at all wavelengths in the visible, thanks to the increased light scattering by the corrugated grating surface. Also, the samples with the grating show additional absorption bands due to the surface plasmon modes. Two different types of surface plasmon modes, SPPs and LSPPs, are identified. The SPPs mode presents an absorption band whenever the grating coupling condition is satisfied. An independent computation of the grating coupling condition shows excellent agreement with the observed absorption band positions due to the SPPs mode. The LSPPs mode is found to show only small shift as a function of active layer thickness in contrast to the SPPs mode which shows large red shift with increasing thickness. The two types of modes exhibit strong mixing near the thickness of 30 nm, causing significant changes in the mode profiles. The LSPPs mode, which is relatively insensitive to the active layer thickness, is located at the absorption edge of the active material and thus made a substantial contribution to absorption enhancement for active layer thicknesses of 50 nm or larger while the SPPs modes produced new absorption bands in the below-bandgap region. This study shows the presence and interplay between the two different types of modes in the plasmonic grating patterned on the back-electrode. The full optimization for the energy conversion enhancement for this OPV device, which is currently underway, must take into account the interaction between the multiple modes present in the structure.

3 Surface Plasmon enhanced upconversion for photovoltaic applications

3.1 Introduction

Limited by the material bandgap, the traditional semiconductor photovoltaic (PV) devices can harvest only the visible solar photons. Large amount of solar energy stored in the near-infrared photons, which is below the semiconductor bandgap, cannot be utilized by the traditional photovoltaics. People have tried different approaches to address the mismatch of solar spectrum and PV absorption spectrum. One example is what has been discussed in last chapter. By placing the surface plasmon resonance at the band edge of organic semiconductor, the absorption can extend over the band edge. The overall absorption enhancement can reach around 10%. Besides extending the absorption band of semiconductor, another approach is to engineer the solar spectrum by using upconversion material. It is a kind of material that can convert multiple low-energy near-infrared photons into one high-energy visible photon that semiconductor PV devices can well absorb. The research of upconversion material formed by optically active ions has a long history stretching back to the mid-1960s[58]. Generally, the ions are successively pumped multiple times *via* the long-lived intermediate energy levels from which they are excited further into the higher energy levels either by directly absorbing another photon or through energy transfer from the nearby sensitizer ions. The former is called excited state absorption (ESA) and the latter energy transfer upconversion (ETU). In either case, the ions emit photons with frequencies higher than that of the incident photon. Compared to other frequency upconversion techniques, e.g. high harmonic generation, parametric oscillation and two-photon absorption, the ETU and ESA are known to be far more efficient[58]. Thanks to the relatively high efficiency,

these processes do not require phase matching and can be excited by incoherent light source at low intensities. With the advance of nanocrystals research in recent years, high quality upconversion nanoparticles can be prepared routinely, spawning a wide range of new applications in solar energy conversion[59], lighting[60], displays[61], biosensing[62], and biomedical imaging[63], [64]. More recently, novel applications such as security ink[65] and photoswitching[66] are also being explored.

In the application of upconversion materials to PV devices, the relative enhancement of the solar cells' short-circuit currents by up to 0.55% has been achieved[67], [68], a 40-fold improvement compared to the first reported value[69] in 2011. Though great improvement has been made, the enhancement of PV performance is still weak due to the low efficiency of upconversion materials. One of the most efficient upconversion materials is $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$, which is typically prepared in powder form and exhibits upconversion efficiencies up to 4% at around 10 W/cm^2 excitation intensity[70]. For photovoltaic applications such as organic photovoltaics device, nanometer size upconversion particles are required. With the reduced size, the overall luminescence efficiency decreases dramatically due to the more severe quenching to surface defects[71]. Plasmonics offer a promising avenue to overcome this problem and achieve high efficiency. By placing the plasmon resonance at the excitation frequency, both the absorption and energy transfer processes can be enhanced[6], [72]. The enhancement of upconversion PL can be several hundredfold[73], [74]. Surface plasmon can also enhance the emission process, if the plasmon resonance is aligned with the emission frequency[75], through the well-known Purcell effect[18]. There have been many reports on plasmonic enhancement of upconverted luminescence, which has been thoroughly reviewed recently[7], [76]. Despite the

rapidly increasing number of publications in this subject, the precise mechanism of plasmon enhancement for the upconversion processes is not yet fully understood[6], [7], [72].

In this chapter, I will systematically study the plasmon enhancement mechanism of the upconversion processes in $\text{NaYF}_4:18\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ upconversion nanoparticles (UCNPs) deposited on a plasmonic nanograting structure. The steady state PL measurements demonstrate up to 16-fold and 39-fold enhancement on green and red emission, respectively. Combined with the rate equations analysis, I reveal that the PL enhancements originate from the 3-fold absorption enhancement and 1.6-fold enhancement on energy transfer upconversion coefficients. Later, I will discuss the study on the dynamics of upconversion processes by transient PL analysis. I proposed the method to directly measure the internal upconversion efficiency (IUCE), and observed 1.6-fold enhancement of IUCE from plasmonics. The highest IUCE we have achieved is 56% with plasmonics, and 36% in absence of plasmonics. I also measured the energy transfer upconversion (ETU) rate, and observed 2.7-fold enhancement of ETU rate by plasmonics. To the best of my knowledge, this is the first report of measured ETU rate and internal upconversion efficiency. My work elucidates the role of plasmon resonance in the ETU system. The clear understanding and quantification of the plasmon enhancement of energy transfer process paves the way for more advanced design of plasmonic enhanced upconversion luminescence materials.

3.2 Steady-state photoluminescence study

3.2.1 Sample preparation and characterization

The $\text{NaYF}_4:18\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ upconversion nanoparticles were synthesized by the co-precipitation method[77], [78]. As shown in the transmission electron micrographs (TEM) in Fig. 3.1(a), the nanoparticles were regular hexagonal platelets, indicating the formation of β -phase NaYF_4 nanocrystals. The mean lateral size was 32 nm. The Yb^{3+} and Er^{3+} doping densities were 18% and 2%, respectively. The UCNPs were of good optical quality and exhibited strong upconverted luminescence under the excitation at 980 nm. The as-synthesized UCNPs are covered with oleic acid and thus not water-soluble. To make them water-soluble and also to make the nanoparticle surface negatively charged, we coated the nanoparticles with poly(maleic anhydride-*alt*-1-octadecene) (PMAO). The Inset of Fig. 3.1(a) shows thin and uniform coating of PMAO on UCNPs. The mean coating thickness was 2 nm. The PMAO coated UCNPs can then be deposited uniformly in the layer-by-layer (LBL) fashion with precisely controlled thickness, as shown in the Appendix. To study the plasmon enhancement effect, a one-dimensional (1D) silver nanograting was fabricated on a 200 nm thick silver film by the nano-imprint lithography (NIL). Since the fabrication process involved oxygen plasma treatment as described in section 2.4, a 10 nm thick gold layer was first deposited on the 200 nm thick silver film in order to prevent oxidation of silver. The subsequent nano-patterning by NIL and lift-off resulted in 20 nm thick and 410 nm wide silver lines with a period of 830 nm, as shown in the scanning electron micrograph (SEM) in Fig. 3.1(b). On the silver nanograting, a 30 nm thick Si_3N_4 spacer layer was first deposited by the chemical vapor deposition to alleviate luminescence quenching by the metal surface. And then three monolayers of UCNPs were deposited by the LBL method using

poly(allylamine hydrochloride). The thickness of the LBL UCNP layers was measured by atomic force microscopy and the three monolayers of UCNPs were found to be 90 nm thick (Data presented in the Appendix). The nanograting parameters were chosen by the finite element modeling so that the structure should support surface plasmon mode at 980 nm after the deposition of Si_3N_4 spacer layer and three monolayers of UCNPs. For comparison's sake, reference samples were also prepared by depositing a 30 nm thick Si_3N_4 and three monolayers of UCNPs on the flat silver surfaces with 10 nm thick gold film on top. Metal surface can affect luminescence in three different ways: plasmon enhancement, quenching, and reflection of backward emitted luminescence. The flat metal surface was chosen as reference because it presents the same degree of quenching and reflection as the nanograting surface. The difference between the reference and nanograting samples should therefore be solely due to the plasmon effect.

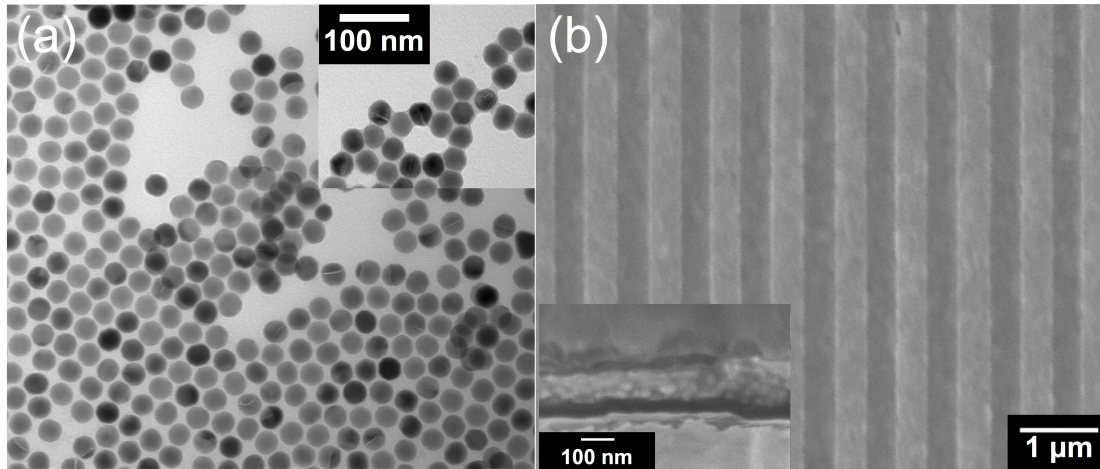


Figure 3.1 (a) TEM of as-synthesized β -phase $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ UCNPs. The mean lateral size was 32 nm. The inset shows the TEM of PMAO-coated UCNPs showing uniform 2 nm thick coating. The scale bar applies to both TEM images. (b) SEM of silver nanograting with period of 830 nm and line width of 410 nm. The inset shows the cross-sectional SEM of grating- Si_3N_4 -UCNPs. The black layer in the middle is 30 nm Si_3N_4 coating sitting on top of the nanograting. Above the Si_3N_4 layer are the three monolayers of

UCNPs. The thickness was consistent with the atomic force microscopy measurements. To acquire good quality images, a thick gold overlayer was deposited on top of UCNPs for this sample.

The fabricated samples were characterized by reflectance and PL spectroscopy. The reflectance spectra were taken at normal incidence and the samples did not have any transmission due to the thick silver substrate. As shown in Fig. 3.2(a), the as-fabricated silver nanograting exhibited a well-defined dip at 850 nm due to the coupling to the surface plasmon mode. Upon depositing the Si₃N₄ spacer layer and three layers of UCNPs, the plasmon peak shifted to 980 nm, as designed. The red shift is due to the increased effective index of the dielectric half-space and is consistent with the theory for surface plasmon modes on the dielectric-loaded metal surface[52], [54], [79]-[83]. The background reflectance was reduced to around 0.75 after UCNP deposition, indicating some light scattering due to the roughness of the UCNP surface. However, the UCNP film was uniform enough to preserve a strong and well-defined dip due to the surface plasmon resonance. To further confirm the existence of surface plasmon mode and to estimate the anticipated field enhancement effect, I performed the finite element modeling using the structural parameters as measured by SEM shown in Fig. 3.1(b). The gold and silver dielectric functions were based on the experimentally measured bulk values[56], [84], [85], except that the imaginary part was increased to account for the increased loss due to electron scattering by the grain boundaries[77], [83]. As shown in Fig. 3.2(a), an excellent agreement was found between experimental and simulated reflectance spectra, indicating the high optical quality of the samples used in this study. Once the presence of surface plasmon mode was confirmed experimentally, I conducted PL spectroscopy using 980 nm laser excitation. As shown in Fig. 3.2(b), both the UCNPs on nanograting and the reference sample on flat silver surface exhibited green and red emission bands, which were attributed to the $^4S_{3/2}, ^2H_{11/2} \rightarrow ^4I_{15/2}$

and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions of Er^{3+} ion (Fig. 3.3), respectively. However, the UCNPs on nanograting showed much stronger PL intensities under all excitation power densities. Fig. 3.2(b) shows the PL spectra taken under the excitation power density of 1 kW/cm^2 , which exhibited 16x and 39x enhancements in the green and red PL peak intensities, respectively. The enhanced PL intensities in the UCNPs on nanograting are direct evidences of the local field enhancement effect due to surface plasmon. For completeness, I have also measured upconverted luminescence from the UCNPs deposited on a glass substrate. The UCNPs on nanograting exhibited up to 25x and 31x enhancement in green and red emission, respectively, demonstrating that the UCNPs on nanograting show overall enhancement of upconversion efficiency over both metallic and non-metallic surfaces.

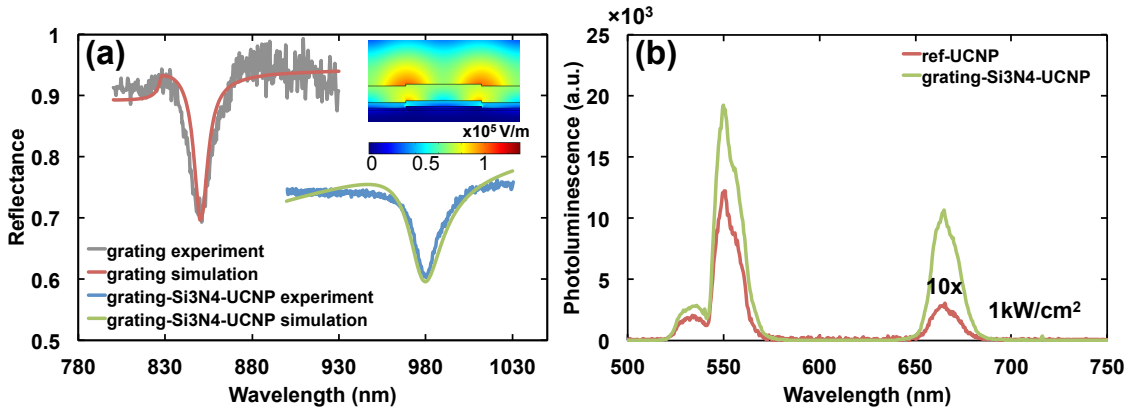


Figure 3.2 (a) Experimental reflectance spectra of as-fabricated nanograting (grey) and nanograting-Si₃N₄-UCNP structure (blue). The simulated reflectance spectra for the two structures are also plotted with red and green lines. The inset shows the field profile at the resonance wavelength for the nanograting-Si₃N₄-UCNP sample under normally incident plane wave excitation with a power density of 1.2 MW/m^2 . (b) PL spectra of reference sample on flat metal film (red) and nanograting-Si₃N₄-UCNP sample (green). The excitation wavelength and power density were 980 nm and 1 kW/cm^2 , respectively. PL intensity of reference UCNP sample is magnified by 10-fold for better visualization.

3.2.2 Steady-state rate equation analysis

The ETU mechanism for luminescence upconversion in $\text{Yb}^{3+}, \text{Er}^{3+}$ co-activated materials has been studied previously[52], [79]-[83]. The major processes are shown schematically in Fig. 3.3. Most of the incident light is absorbed by the Yb^{3+} ions because they have nine times higher doping density in our samples and exhibit much larger absorption cross-section than the Er^{3+} ions[84]-[86]. The absorption of the incident photon thus excites the Yb^{3+} ion into the $^2\text{F}_{5/2}$ level, from which the Yb^{3+} ion decays back to the ground level, $^2\text{F}_{7/2}$, via the Förster energy transfer process, exciting a nearby Er^{3+} ion into the $^4\text{I}_{11/2}$ level. If the energy transfer takes place one more time before the excited Er^{3+} ion decays back to the ground state, the Er^{3+} ion is excited to the $^4\text{F}_{7/2}$ level and then quickly decays non-radiatively to the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels from which the green luminescence occurs. A fraction of Er^{3+} ions in the $^4\text{S}_{3/2}$ state would decay non-radiatively into the slightly lower $^4\text{F}_{9/2}$ level where the red luminescence originates. An additional path for the red emission is for the Er^{3+} ion in $^4\text{I}_{11/2}$ level to decay non-radiatively into the $^4\text{I}_{13/2}$ level and then get excited to the $^4\text{F}_{9/2}$ level by the Förster energy transfer from a nearby Yb^{3+} ion. There are other processes that compete with the ETU process such as radiative and non-radiative decays from $^2\text{F}_{5/2}$ of Yb^{3+} and $^4\text{I}_{11/2}$ of Er^{3+} , back energy transfer from Er^{3+} to Yb^{3+} , and cross-relaxation of Er^{3+} ion pairs. The cross relaxation of Er^{3+} ions offers a major quenching mechanism at high Er^{3+} concentrations[83], [86]. Furthermore, there are three-photon upconversion processes, resulting in blue emission and also contributing to the green and red emission[82], [86]. However, it is expected and has been experimentally demonstrated that the three-photon processes make much smaller contributions than the two-photon processes and are therefore omitted in our analysis of green and red luminescence intensities[82], [87], [88].

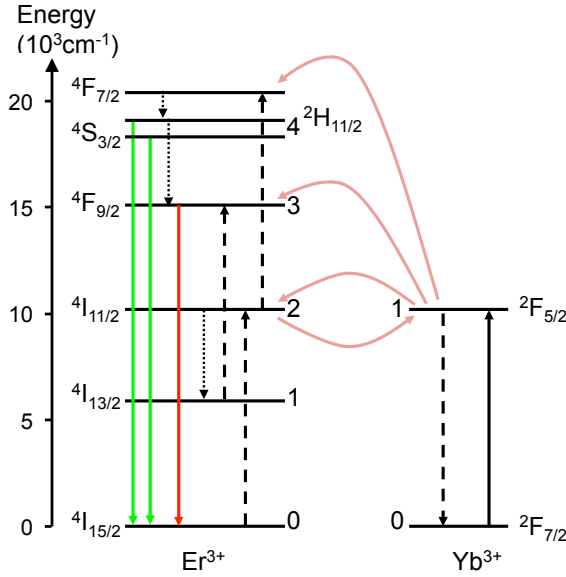


Figure 3.3 Energy levels of Yb^{3+} and Er^{3+} ions relevant to the energy transfer upconversion process. Initial absorption is indicated by the black solid line arrow, subsequent energy transfer processes by the dashed arrows, non-radiative relaxations by dotted arrows and the final upconverted luminescence by the green and red arrows.

Upconverted luminescence is known to exhibit distinct power-law dependence on the excitation power density[86], [89]. In the weak excitation limit, the upconverted luminescence intensity is proportional to the k^{th} power of the excitation power density where k is the number of upconversion steps involved. In the strong excitation limit, however, the upconverted luminescence intensity is simply proportional to the excitation power density. The distinction between the weak and strong excitation conditions is made by comparing the rates of upconversion and decay. For a given energy level in the upconversion system, we anticipate two competing processes: upconversion to a higher energy level and decay (radiative and non-radiative) into a lower energy level. In the weak excitation limit, decay process is dominant while, in the strong excitation limit, upconversion process dominates. This approximation greatly

simplifies the rate equations and leads to the distinct power dependence described above, which has also been verified experimentally[86], [90].

To investigate the plasmonic effect on the excitation power dependence, I measured the visible emission intensity under various excitation power densities. Fig. 3.4 shows the power dependence of the green and red emission intensities for UCNPs on silver nanograting and on flat silver film (reference sample). For both green and red emission, the luminescence intensity exhibited quadratic and linear dependence on the excitation power density at low and high power densities, respectively. This is consistent with the previous report[86], [89], [91]-[96] and indicates the upconversion processes for both green and red emission are dominated by two-step ETU with negligible contributions by three-step processes. The power dependence of UCNPs on silver nanograting was identical to that of the reference sample for both green and red emission, except that the transition between weak and strong excitation regimes occurred at lower power densities. This result clearly shows that the plasmon resonance increases the local optical power density. From Fig. 3.4(a) and (b), the power densities at which the transition between weak and strong excitation regimes occurs were estimated to be 3.6 and 5.0 times lower for the green and red emission from the nanograting sample compared to the reference sample. These numbers provide an estimate of how much local optical power density is enhanced in the plasmonic grating sample and agree well with the absorption enhancement factor derived later.

The observed shift in the power dependence consequently results in power dependent enhancement factor, which is defined as the ratio of integrated emission intensity between UCNPs on nanograting and reference samples. It should be noted that I calculated the emission pattern for the nanograting and reference samples as described in Appendix and found the difference negligibly small. The observed PL enhancement is therefore the actual enhanced

UCNP emission. As shown in Fig. 3.4(c), the enhancement factor for green emission varied from 3.1 to 16.0 while the red emission enhancement factor changed from 4.2 to 38.8. We note that the enhancement factor is independent of excitation power in the low and high power limits while it changes rapidly in the intermediate region. Therefore, when discussing the plasmon enhancement effects in upconversion materials, it is imperative to specify the excitation power density and identify whether the measurements were taken in the weak, intermediate or strong excitation regimes. The inherent power dependence of enhancement factor explains in part the wide variations in the reported values of enhancement factors found in the literature.

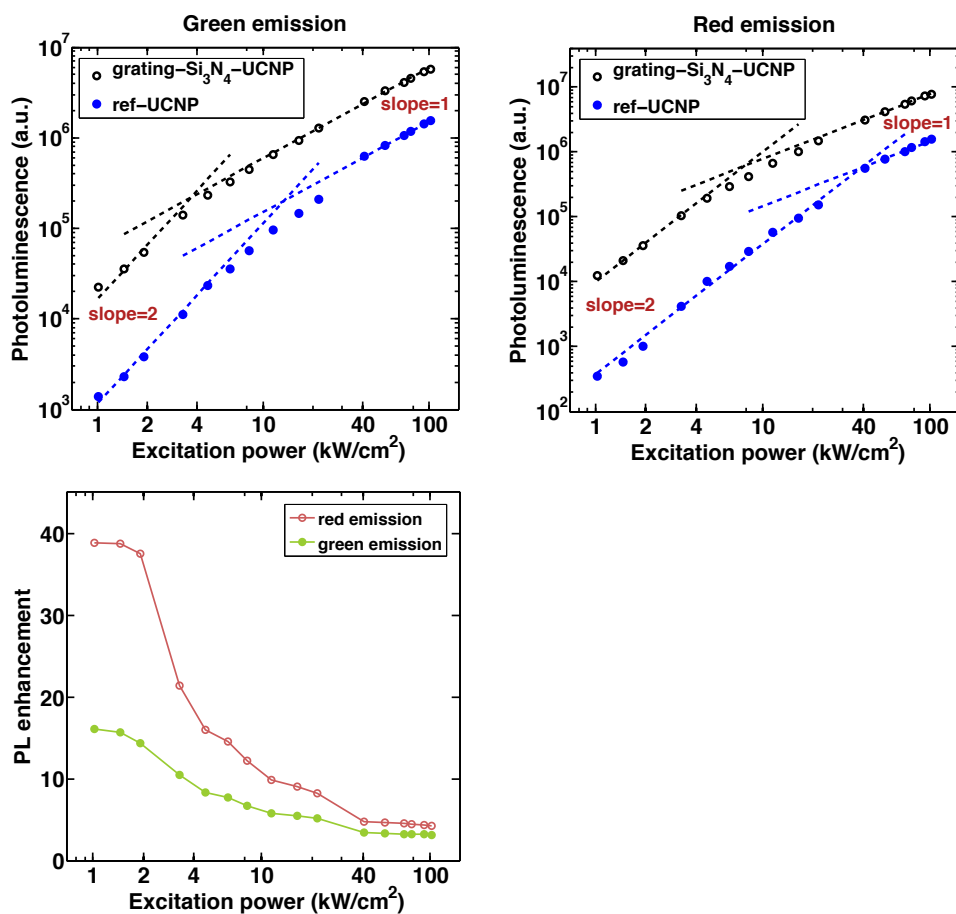


Figure 3.4 (a) Green and (b) red photoluminescence intensities under various excitation power densities. The UCNP on silver nanograting is denoted with black open circles while the reference sample on flat

metal film is represented by blue filled circles. The blue and black dash lines are obtained by the least-square fitting with the slopes of 1 and 2 as denoted. (c) Enhancement factors of the green (green filled circles and line) and red (red open circles and line) upconverted luminescence as a function of the excitation power density.

For complete understanding of the plasmon enhancement mechanism, I set up rate equations describing all key processes affecting the ETU mechanism. In the rate equations, the $^4F_{7/2}$ level of Er^{3+} is not included as the relaxation from the $^4F_{7/2}$ level to the lower-lying $^2H_{11/2}$ and $^4S_{3/2}$ levels is known to be extremely fast[89], [96], [97]. Also, the $^2H_{11/2}$ and $^4S_{3/2}$ levels are close enough to be considered as a single level. The complete set of rate equations is then written as,

$$\frac{dN_{D1}}{dt} = \sigma\Phi N_{D0} - W_{D10}N_{D1} + c_{Bd2}N_{A2}N_{D0} - c_{Fd2}N_{D1}N_{A0} - c_{d3}N_{D1}N_{A1} - c_{d4}N_{D1}N_{A2} \quad (3.1)$$

$$\frac{dN_{A1}}{dt} = W_{A21}N_{A2} - W_{A10}N_{A1} - c_{d3}N_{D1}N_{A1} \quad (3.2)$$

$$\frac{dN_{A2}}{dt} = c_{Fd2}N_{D1}N_{A0} - c_{Bd2}N_{A2}N_{D0} - c_{d4}N_{D1}N_{A2} - W_{A20}N_{A2} - W_{A21}N_{A2} \quad (3.3)$$

$$\frac{dN_{A3}}{dt} = W_{A43}N_{A4} + c_{d3}N_{A1}N_{D1} - W_{A30}N_{A3} \quad (3.4)$$

$$\frac{dN_{A4}}{dt} = c_{d4}N_{D1}N_{A2} - W_{A40}N_{A4} - W_{A43}N_{A4} \quad (3.5)$$

$$N_D = N_{D0} + N_{D1} \quad (3.6)$$

$$N_A = N_{A0} + N_{A1} + N_{A2} + N_{A3} + N_{A4} \quad (3.7)$$

Here N_i is the density of ions in the energy level i . The subscripts D1 and D0 represent the $^2F_{5/2}$ and $^2F_{7/2}$ levels of donor (Yb^{3+}), respectively, and A4, A3, A2, A1, and A0 indicate the $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ levels of acceptor (Er^{3+}), respectively. W is the decay rate and the subscript indicates the initial and final states of the transition. For example, W_{D10} is the decay rate of donor

ion from D1 to D0 state. c_{d2} , c_{d3} and c_{d4} are the energy transfer coefficients for the Förster energy transfer processes between the donor and the acceptor in A2, A3 and A4 levels, respectively. The additional subscripts, F and B, in the c_{d2} coefficient indicate the forward (donor to acceptor) and backward (acceptor to donor) energy transfers. Finally, N_D and N_A are the doping densities of donor and acceptor, respectively, $\sigma \approx 0.24 \times 10^{-20} \text{ cm}^2$ is the absorption cross-section of the donor ion[98] averaged over different polarizations at 980 nm, and Φ is the incident light flux. It is noted that the three-photon ETU processes are not included in the rate equations as they should in general have much lower probability than the two-photon mechanism[70], [90], [99]. Also omitted for simplicity are the transitions from the $^4S_{3/2}$ level to the intermediate energy levels, $^4I_{11/2}$ and $^4I_{13/2}$, which are generally weak although they may become significant when $^4S_{3/2}$ population is high. Furthermore, I consider only the backward transfer from the acceptor $^4I_{11/2}$ level to donor as the lifetimes of the higher excited states of the acceptor are so short that back transfer is negligible. Finally, the decay rate, W , should in general include the rate of both radiative and non-radiative decays. In conventional $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ samples, the major non-radiative decay channel is multiphonon emission, but thanks to the small phonon energy of the fluoride host, the non-radiative decay rate is usually small. Thus W is typically replaced with the radiative decay rate. In our case, however, the UCNP are in close proximity of metal surface and the energy transfer to metal offers a highly efficient non-radiative decay channel and therefore non-radiative decay rate should not only be included but could very well dominate. This was confirmed by the time-resolved PL spectroscopy. UCNP exhibit infrared luminescence due to the direct radiative decay from $^2F_{5/2}$ to $^2F_{7/2}$ and also from $^4I_{11/2}$ to $^4I_{15/2}$ levels. Since these emission bands are too close to the excitation laser, we could not fully resolve the entire emission band. In fact, even after strong attenuation by a sharp-edged long-pass filter, strong

laser peak was persistent. Nevertheless, I was able to observe the long wavelength tails of the UCNP emission. As shown in Fig. 3.5(a), the emission band peaking at 1005 nm was observed only from the UCNP containing samples but not from the scattered laser light, confirming this emission band originates from the UCNPs. Then, the luminescence decay was monitored at 1005 nm followed by a pulsed excitation. I used a train of square pulses with a pulse width of 23 ms and a period of 42 ms. Both the pulse width and the interval between two successive pulses were chosen to be much longer than the rise and decay times of the upconverted luminescence so that the system reaches steady state before the excitation pulses are turned on and off. As shown in Fig. 3.5(b), the UCNPs deposited on glass exhibited an exponential decay with a lifetime of 1.7 ms. This value is consistent with the radiative decay time previously reported in the literature[72], [89], [91]-[96], [100]-[102] and is indicative of small non-radiative decay and high material quality. The UCNPs on nanograting and flat silver film both showed much faster decay with lifetimes of 201 and 199 ms, respectively. As shown later, the Purcell factor is close to unity. Thus, the large reduction in decay time is due to the luminescence quenching by metal, which appears to persist despite the use of the 30 nm Si_3N_4 spacer layer. An important point, however, is that both the UCNPs on nanograting and flat silver film exhibited the same decay time. Thus, W_{A20} and W_{D10} , dominated by non-radiative energy transfer to metal, remain the same in both the nanograting and the reference samples.

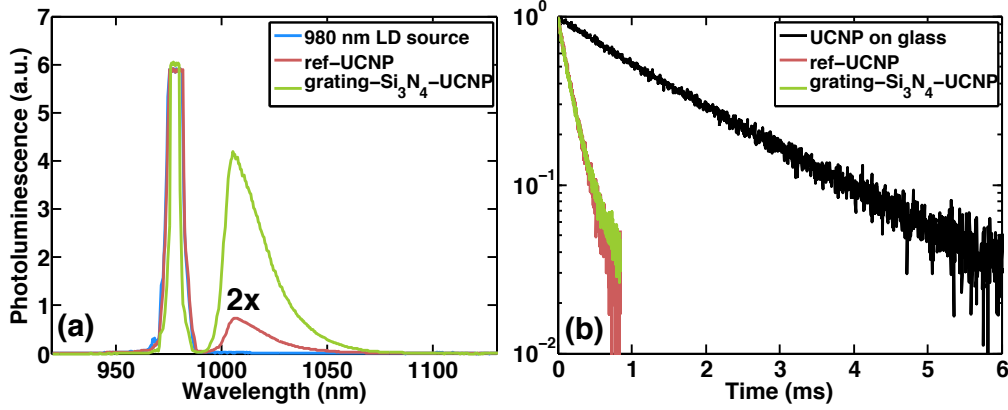


Figure 3.5 (a) Photoluminescence spectra of a 980 nm laser diode source (blue, magnified by 2x), reference sample on flat metal film (red, magnified by 2x) and nanograting sample (green). The UCNP emission profile is modulated by a 997 nm long pass edge filter, which attenuates the scattered laser light. (b) Photoluminescence decay at 1005 nm for the UCNP on glass (black), reference sample (red) and nanograting sample (green) under 1.9 kW/cm² excitation power density.

Since the rate equations given above are rather unwieldy, even after the omission of three-photon processes, it is profitable to seek for further simplifying approximations. Many groups have ignored the red emission entirely[79], [81], [85], [89], [91], [96], [97], [103], [104]. Others assumed fast equilibrium between the $^2F_{5/2}$ level of Yb³⁺ and the $^4I_{11/2}$ level of Er³⁺[70], [97], [99], [103], [105]. And yet other groups ignored the back energy transfer from Er³⁺ to Yb³⁺[72], [93], [96], [100]-[102], [106]. However, the justifications for these approximations are often dubious. As shown in Fig. 3.2 and 3.4, red emission is clearly not negligible and is dominant at high excitation power densities. The assumption of fast equilibrium requires the c_{Fd2} and c_{Bd2} coefficients are so large that the forward and backward energy transfer rates are much greater than the radiative and non-radiative decay rates. Ignoring backward energy transfer means $c_{Fd2} \gg c_{Bd2}$, which is at odds with the assumption of fast equilibrium. The problem lies in the difficulty in directly measuring the energy transfer coefficients. There is naturally a dearth

of data on energy transfer coefficients. However, the few that reported the values of energy transfer coefficients indicate that c_{Fd2} and c_{Bd2} are of the same order of magnitude[85], [91], [97], [103], [104], [106], [107] and the energy transfer rates may be comparable to the decay rates[97], [103], [105]-[110]. Although the values of energy transfer coefficients depend strongly on the doping densities and the host material, the approximations mentioned above appear to be poorly justified and I therefore proceed with the full set of equations (3.1)~(3.7) to investigate the behaviors in the weak and strong excitation limits. The details on how to obtain steady-state solutions of the rate equations under continuous-wave excitation are given in the Appendix. The essence of the approximations made for weak and strong excitation limits is to consider the competition between the upconversion processes and decay processes for the intermediate energy levels, $^2F_{5/2}$ and $^4I_{11/2}$. In the weak excitation regime, decay processes dominate while the upconversion processes become dominant in the strong excitation regime. These approximations allow significant simplifications and offer simple and revealing solutions. In the weak excitation limit, the green and red photon emission rates (in units of per volume per time) are given as,

$$\Phi_G = \frac{W_{A40}}{W_{A4}} \frac{c_{d4} c_{Fd2} N_A N_D}{c_{Bd2} W_{D10}^2} \cdot (\sigma\Phi)^2 \quad (3.8)$$

$$\Phi_R = \left(\frac{W_{A43} c_{d4}}{W_{A4}} + \frac{W_{A21} c_{d3}}{W_{A10}} \right) \frac{c_{Fd2} N_A N_D}{c_{Bd2} W_{D10}^2} \cdot (\sigma\Phi)^2 \quad (3.9)$$

Here the W_{A4} is the total decay rate of energy level A4, $W_{A4} = W_{A40} + W_{A43}$. Equations (3.8) and (3.9) clearly show the quadratic dependence on the incident photon flux, which is a consequence of the two-photon process responsible for upconversion and is also consistent with the experimental data in Fig. 3.4. In addition, they show the upconverted luminescence intensity should increase linearly with the donor and acceptor densities. Also, the upconverted

luminescence intensity varies linearly with the energy transfer coefficients, c_{Fd2} and c_{d4} , and inversely with c_{Bd2} and the square of donor decay rate, W_{D10} . In the strong excitation limit, the green and red photon emission rates are found to be,

$$\Phi_G = \frac{W_{A40}}{W_{A4}} \frac{N_{D0}}{2} \sigma \Phi \quad (3.10)$$

$$\Phi_R = \frac{W_{A43}}{W_{A4}} \frac{N_{D0}}{2} \sigma \Phi \quad (3.11)$$

Equations (3.10) and (3.11) show the linear power dependence on the excitation power density as observed in Fig. 3.4. Also, it is important to note that the upconverted luminescence intensity depends only on the donor density and excitation power density but not on any of the energy transfer coefficients since, in the strong excitation limit, the energy transfer rate is so fast that the upconversion is limited by the absorption by the donor ion.

The simplified expressions in equations (3.8)~(3.11) provide the basis for determining the plasmon enhancement effects on the various processes involved in upconversion. The enhancement factors, F_{weak} and F_{strong} , for the green luminescence intensity in the weak and strong excitation limits can now be written as

$$F_{\text{weak}} = \frac{F_{d4} F_{Fd2} F_a^2}{F_{Bd2} F_p^n} \quad (3.12)$$

$$F_{\text{strong}} = F_a \quad (3.13)$$

where F_{Fd2} , F_{Bd2} and F_{d4} are the enhancement factors for the energy transfer processes represented by the coefficients c_{Fd2} , c_{Bd2} and c_{d4} , respectively, F_a is the absorption enhancement factor, and F_p is the Purcell factor, which is the enhancement factor for the radiative decay rate. The exponent, n , for the Purcell factor in equation (3.12) is either 0 or 2, depending on whether the

donor decay is dominated by non-radiative or radiative channels. According to equation (3.13), the enhancement in the strong excitation limit is entirely due to the absorption enhancement. From Fig. 3.4(c), the enhancement factors for the green and red emission in the strong excitation limit are 3.1 and 4.2, respectively. Ideally, the enhancement factors should be the same for both green and red emissions. The discrepancy is attributed to the red emission excited by the three-photon processes, which could become non-negligible in the strong excitation limit but are not included in our rate equation analysis. I therefore consider the enhancement factor for the green emission to be the more accurate value for the absorption enhancement, $F_a = 3.1$. Since the time-averaged absorbed power is given by $U_a = \frac{1}{2} \int \omega \epsilon'' |\mathbf{E}|^2 dV$, where ϵ'' is the imaginary part of the permittivity, the absorption enhancement can be calculated numerically by comparing the $|\mathbf{E}|^2$ integrated over the UCNP layer. For absorption calculation, the obtained steady state field distribution at 980 nm is shown in the inset of Fig. 3.2. The field profile shows surface plasmon modes with enhanced local field strength. The resultant absorption enhancement in the UCNP layer on nanograting structure compared to the reference sample on flat silver film was 2.8 which was in good agreement with the experimentally observed green enhancement factor in the strong excitation limit and thus offers a strong support for our assertion that the green enhancement is due entirely to the absorption enhancement.

Now let us turn our attention to equations (3.8) and (3.12) for the green emission in the weak excitation limit. Since the green emission rate has quadratic dependence on the incident power, the overall enhancement factor should depend on F_a^2 . For the donor decay rate W_{D10} in equation (3.8), Fig. 3.5(b) showed the decay rate is determined mainly by the non-radiative decay rate with an effective lifetime of around 200 μs which is over 8 times smaller than the

radiative decay time of UCNP on glass substrate. Therefore, the decay processes will remain predominantly non-radiative even if there is a modest increase in radiative decay rate by the Purcell effect. As discussed later, the Purcell factor is close to unity in our system. The value of W_{D10} would therefore remain unaffected by the plasmon resonance and we choose $n = 0$ in equation (3.12). Since the branching ratio, W_{A40}/W_{A4} , and the doping densities, N_D and N_A , should be independent of the excitation power, the only remaining factors in equation (3.8) are the energy transfer coefficients, c_{Fd2} , c_{Bd2} and c_{d4} , whose enhancement factors are denoted as F_{Fd2} , F_{Bd2} and F_{d4} in equation (3.12). Since the experimental data tell us $F_{strong} = 3.1$ and $F_{weak} = 16.0$, we find $F_{Fd2}F_{d4}/F_{Bd2} = 1.7$.

To continue the discussion on the enhancement factors for the energy transfer coefficients, consider the Förster energy transfer rate for a donor-acceptor pair in a dispersive and absorbing medium given by

$$W_{ET} = \int d\omega \sigma_A(\omega) \sigma_D(\omega) \tilde{w}(\omega) \quad (3.14)$$

where σ_A and σ_D are the free-space absorption and emission spectra of acceptor and donor, respectively [106], [111], [112]. The information about the medium is contained in $\tilde{w}(\omega)$, which can be expressed in terms of the dyadic Green function as follows.

$$\tilde{w}(\omega) = \frac{2\pi}{\hbar^2} \frac{\omega^2}{\epsilon_0 c^2} \left| \mathbf{d}_A^* \cdot \mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{d}_D \right|^2 \quad (3.15)$$

Here, $\mathbf{d}_A$ and $\mathbf{d}_D$ are the dipole moments of acceptor and donor respectively; $\mathbf{r}_A$ and $\mathbf{r}_D$ indicate the positions of acceptor and donor respectively. Using this formalism, it has been shown theoretically that the Förster energy transfer rate can be enhanced near the plasmon resonance [106], [107], [113]. The rigorous evaluation of the dyadic Green function is non-trivial and the theoretical works have so far been carried out mostly for highly symmetric shapes like

planar surface, sphere and ellipsoid[106]-[110], [114], [115]. An earlier study observed enhanced Förster energy transfer rate in optical cavities and attributed it to the enhanced local density of states (LDOS) to which the donor emission rate is directly proportional[106], [107], [111]. In terms of the dyadic Green function, however, the emission rate of a dipole is given by,

$$W_{SE} = \frac{2\omega^2}{\hbar\epsilon_0 c^2} [\mathbf{d}_D^* \cdot \text{Im} \mathbf{G}(\mathbf{r}_D, \mathbf{r}_D, \omega) \cdot \mathbf{d}_D] \quad (3.16)$$

where Im indicates the imaginary part[112], [113], [116]-[121]. For a small donor-acceptor distance, $\mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega)$, may be similar to $\mathbf{G}(\mathbf{r}_D, \mathbf{r}_D, \omega)$. However, the real part of the dyadic Green function often dominates over the imaginary part and thus the energy transfer enhancement is generally quite different from the emission enhancement. In fact, it has recently been shown that the energy transfer enhancement is not related to the LDOS enhancement[114], [115], [122]. The theoretical studies indicate that the energy transfer enhancement is generally much smaller than the spontaneous emission enhancement[106], [107], [123]. Nevertheless, it has been experimentally observed that the Förster energy transfer rate can be significantly enhanced in the vicinity of plasmonic structures[112], [116]-[121].

In order to properly describe the effect of energy transfer on the upconversion process in the UCNPs where the donor density is very high, we must consider energy transfer among donors. For multipolar interaction mechanism, the energy transfer rate between a donor and an acceptor separated by a distance, r , is given by[122]

$$W_{ET}(r) = \frac{1}{\tau_R} \left(\frac{r_0}{r} \right)^s \quad (3.17)$$

where r_0 is the Förster radius defined as the distance at which the energy transfer rate becomes equal to the radiative decay rate, τ_R is the radiative lifetime of the donor, and $s = 6, 8, 10, \dots$ for

dipole-dipole, dipole-quadrupole, quadrupole-quadrupole interaction, respectively. Taking into account the energy migration over donors, the statistical average of the probability of finding a donor in the excited state at time t is given by [123],

$$\phi(t) = \exp \left[-\frac{t}{\tau_R} - \Gamma \left(1 - \frac{3}{s} \right) \frac{N_A}{N_0} \left(\frac{t}{\tau_R} \right)^{3/s} \right] \quad (3.18)$$

where N_A is the acceptor density and N_0 is the critical density defined as $N_0 = 3/(4\pi r_0^3)$. The second term in the exponent in equation (3.18) represents the non-exponential decay due to the energy migration over donors and the eventual energy transfer to an acceptor. An effective energy transfer time, τ_e , can now be defined as the time the probability function decays to the e^{-1} point,

$$\tau_e = \frac{\tau_R}{\pi} \left(\frac{N_0}{N_A} \right)^2 \quad (3.19)$$

for dipole-dipole coupling, $s = 6$. Or the effective energy transfer rate can be written as,

$$\frac{1}{\tau_e} = \frac{\pi}{\tau_R} \left(\frac{N_A}{N_0} \right)^2 = \frac{\pi}{\tau_R} \left(\frac{r_0}{r_A} \right)^6 = \pi W_{ET}(r_A) \quad (3.20)$$

where r_A is defined similarly to r_0 , $N_A = 3/(4\pi r_A^3)$. Thus, in a system like our UCNPs where the energy migration over donors may be significant, the effective rate of energy transfer rate from an excited donor to an acceptor is proportional to the Förster energy transfer rate for an isolated donor-acceptor pair separated by r_A , the effective distance between two adjacent acceptors.

This effective rate of energy transfer can now be related to the energy transfer coefficients used in the rate equations where the rates of forward transfer from $^2F_{5/2}(\text{Yb}^{3+})$ to $^4I_{11/2}(\text{Er}^{3+})$, backward transfer from $^4I_{11/2}(\text{Er}^{3+})$ to $^2F_{5/2}(\text{Yb}^{3+})$, and upconversion transfer from $^2F_{5/2}(\text{Yb}^{3+})$ to $^4F_{7/2}(\text{Er}^{3+})$ are represented by $c_{Fd2}N_{A0}$, $c_{Bd2}N_{D0}$ and $c_{d4}N_{A2}$, respectively. In the weak

excitation limit where the energy transfer rate enhancement is relevant according to equations (3.12) and (3.13), we have $N_{A0} = N_A$ and $N_{D0} = N_D$ and thus write,

$$\begin{aligned} c_{Fd2}N_A &= \pi W_{ET}(r_A), \quad r_A = \sqrt[3]{\frac{3}{4\pi N_A}} \\ c_{Bd2}N_D &= \pi W_{ET}(r_D), \quad r_D = \sqrt[3]{\frac{3}{4\pi N_D}} \\ c_{d4}N_{A2} &= \pi W_{ET}(r_{A2}), \quad r_{A2} = \sqrt[3]{\frac{3}{4\pi N_{A2}}} \end{aligned} \quad (3.21)$$

Thus, to examine the enhancement of energy transfer coefficients, we can evaluate the energy transfer rates given by equation (3.14) at distances r_A , r_D and r_{A2} , which are the critical distances for the ground state acceptor, ground state donor, and excited state ($^4I_{11/2}$) acceptor, respectively, and defined as $r_A = \sqrt[3]{3/(4\pi N_A)}$, $r_D = \sqrt[3]{3/(4\pi N_D)}$, and $r_{A2} = \sqrt[3]{3/(4\pi N_{A2})}$. From the crystal structure data available in the literature[124], we find $N_D = 1.98 \times 10^{21} \text{ cm}^{-3}$ and $N_A = 2.2 \times 10^{20} \text{ cm}^{-3}$ for doping densities of 18% Yb and 2% Er and from these values we determine $r_D = 0.5 \text{ nm}$ and $r_A = 1.0 \text{ nm}$. The density of excited acceptors, N_{A2} , is given by equation (6.14). However, due to the uncertainties of the various parameter values, we make an approximate estimate by invoking a simple rate equation for a two-level system, which asserts that in the steady state the excitation rate should be equal to the decay rate. The decay rate is given by the measured decay time, $t = 200 \mu\text{s}$, from Fig. 3.5(b). The excitation rate is determined by the excitation power density and the absorption coefficient, $a = 6 \text{ cm}^{-1}$ [70]. Since we are concerned with the weak excitation regime, we use the excitation power density of 1 kW/cm^2 and find the excitation rate of $3 \times 10^{22} \text{ cm}^{-3}\text{s}^{-1}$. Now the density of excited ions is found by simply multiplying the excitation rate with the decay time, $N_{A2} = 6 \times 10^{18} \text{ cm}^{-3}$, which subsequently yields $r_{A2} = 3.4 \text{ nm}$.

Evaluating the energy transfer rate from equation (3.14) calls for numerically calculating the dyadic Green function. Unfortunately, this is extremely challenging especially for small donor-acceptor distances as the real part of the Green function becomes very large. Therefore, instead of directly evaluating the energy transfer rate in the nanograting structure, we conducted model calculations for the energy transfer rates near a flat metal surface for which analytical solutions exist[106]. As shown in the data presented in the Appendix, the Förster energy transfer rates are enhanced at frequencies slightly below the surface plasmon frequency. The enhancement is larger for donor-acceptor pairs placed closer to the metal surface and also for larger donor-acceptor separation distances. The enhancement also depends on the orientations of the donor and acceptor dipole moments. However, in no cases do we observe any enhancement for extremely short donor-acceptor distance of 1 nm or shorter. It is therefore reasonable to assume there is no enhancement in c_{Fd2} and c_{Bd2} or $F_{Fd2} = F_{Bd2} = 1$. We may then further simplify equation (3.12) to

$$F_{weak} = F_{d4} F_a^2 \quad (3.22)$$

and find the enhancement factor for the energy transfer upconversion process to be $F_{d4} = 1.7$. This result is considered reasonable because the enhancement calculated for a flat metal surface in the Appendix shows significant enhancements are possible for a donor-acceptor placed $0.03 \lambda_{sp}$ away from metal surface with donor-acceptor distance of 3~4 nm, which corresponds to our estimate of r_{A2} . Our argument is also consistent with the literature which showed the enhancement of Förster energy transfer rate is larger for larger donor-acceptor distances[108], [125], [126]. In particular, a recent theoretical study on the Förster energy transfer rates in the vicinity of metallic nanoparticle showed that the Förster energy transfer rates remain mostly unperturbed for short donor-acceptor distances but strongly modified for large donor-acceptor

distances[107]. This behavior is understood by considering the two components that contribute to the Green function: direct emission of donor dipole and the reflection from the metal surface. For short distances, the former dominates and the Förster energy transfer rate remains the same. For larger distances, the latter begins to make a significant contribution and the resultant interference between the two components gives rise to the increase or decrease in the Förster energy transfer rate. In our case, the contribution by the metal surface becomes significant enough to result in an enhanced Förster energy transfer rate only for the upconversion energy transfer from $^2F_{5/2}(\text{Yb}^{3+})$ to $^4F_{7/2}(\text{Er}^{3+})$.

Finally I discuss the Purcell factor which describes the enhancement of donor radiative decay rate due to the increased LDOS[18], [127]. The Purcell factor depends on the quality factor and mode volume. The plasmonic grating used in this study has a large mode volume and tends to exhibit small Purcell factor[128]. To precisely evaluate the Purcell factor, I followed the method by Gong *et al.*[128] and obtained $F_p = 1.78$. The details of the calculation are given in the Appendix. It is worth mentioning that a recent study showed the Purcell factor is not equal to the acceleration of radiative decay in plasmonic systems[129]. To check this, I numerically calculated the radiation rate of a point dipole using finite-difference time-domain method. Comparing the radiation rates on a nanograting and in free space, I found an enhancement of 1.8, which agrees well with the independently calculated Purcell factor. We thus conclude the Purcell effect accurately describes the donor emission enhancement in our system. The small Purcell factor validates the use of $n = 0$ in equation (3.12) to derive equation (3.22) as the non-radiative processes should dominate the decay of $^2F_{5/2}$ (D1) level. Based on this analysis, we may conclude the absorption and Förster energy transfer are the two processes contributing to the enhancement of luminescence upconversion. In the strong excitation limit, only absorption enhancement

accounts for the entire upconversion enhancement while in the weak excitation limit both the Förster energy transfer and absorption enhancements contribute. Overall, absorption enhancement plays the most important role in the upconversion enhancement.

3.3 Transient photoluminescence analysis

3.3.1 Transient NIR emission

The NIR emission is important because both the absorption and energy transfer processes take place at this frequency. The dynamics of the intermediate level, from which the NIR PL arises, is ultimately determined by the competition between the ETU rate and the decay rate. By measuring the transient NIR PL for different excitation conditions, we can explore the energy transfer processes and the influence of plasmonics on these processes. The details of transient NIR PL measurement setup are described in the Appendix.

I first describe the rise of the transient NIR PL following the leading edge of the square pulse excitation. The NIR PL rise curves (Fig. 3.6) for both the nanograting and reference samples are fitted well by single exponential functions from which the rise rate W_{D1} can be extracted. It is noted that we normalize the transient NIR PL with the steady state PL intensity, and subtract it from unity so that we may visualize the rise process in a similar fashion to the decay process and extract the relevant rate constants. The rise time is shown in Fig. 3.6 legends for both nanograting and reference samples under various excitation conditions.

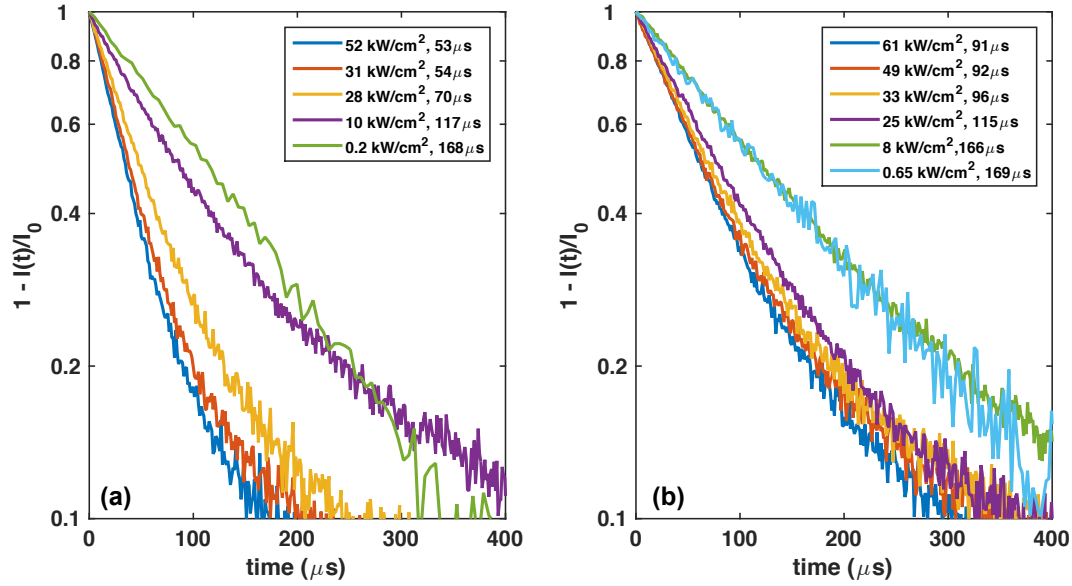


Figure 3.6 Rise of UCNPs emission at 1002 nm on silver nanograting (a) and on silver film (b). The experimentally measured rise curve is normalized to steady state PL intensity and then subtracted from unity, $1 - I(t)/I_0$. The legends describe the excitation power density and the measured rise time.

Under weak excitation, the NIR rise time is close to 170 μs for both nanograting sample and reference sample. As the excitation power density is increased, the rise becomes significantly faster for both nanograting and reference samples. It is important to note that the rise rate of nanograting sample is always faster than that of reference sample under similar excitation conditions, indicating plasmon enhancement of energy transfer rate.

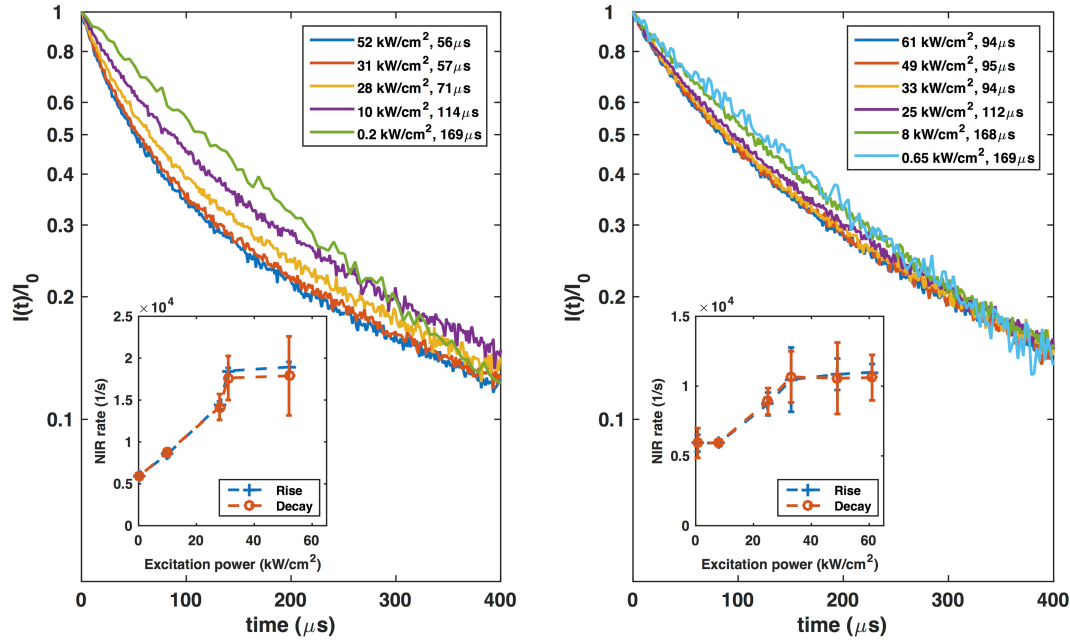


Figure 3.7 Decay of UCNPs emission at 1002 nm on silver nanograting (a) and on silver film (b). All experimental PL decay are normalized to the steady state PL intensity, and plotted in logarithmic scale. The excitation power density and decay time are listed in legends. The insets show the NIR PL rise rate and decay rate fitted from NIR PL rise and decay respectively for nanograting and reference samples under different excitation power densities. The error bar is with 95% confidence bounds.

In addition to the measurement of transient NIR PL rise process, I also measured the decay of NIR PL following the trailing edge of the square pulse excitation. The measured PL decay is normalized to the steady state PL intensity, and shown in semi-log plots in Fig. 3.7. Again, we observe faster decay with stronger excitation. Unlike the rise process, however, the decay starts with single exponential but deviates from it more quickly. For this reason, only the very beginning of the decay has to be fitted with an exponential function to extract the decay time, which inevitably contains larger uncertainty. They are shown in Fig. 3.7 legends for both nanograting and reference samples. The decay rate defined as the inverse of decay time is plotted together with the rise rate W_{DI} in the inset of Fig. 3.7. It is clear that the decay rate is always equal to the rise rate under the same excitation conditions for each sample. As shown later, a

more detailed analysis reveals that the initial part of rise and decay of transient NIR PL represent exactly the same physical processes. However, the rise of transient NIR PL follows single exponential curve for a longer time period, as explained in more detail in the supplementary information, resulting in better fitting quality. Therefore, it is preferable to analyze the rise of transient NIR PL for the energy transfer processes study.

For complete understanding of the plasmon enhancement mechanism, I analyze the transient rate equations (3.1)~(3.7). The NIR PL as shown in Fig. 3.5(a) may come from the radiative decay of both the donor (Yb^{3+}) ions in D1 ($^2\text{F}_{5/2}$) level and the acceptor (Er^{3+}) ions in A2 ($^4\text{I}_{11/2}$) level. The population of D1 and A2 levels is described by equations (3.1) and (3.3), respectively. Combining these two rate equations we get the complete description of the transient NIR PL:

$$\frac{d(N_{D1} + N_{A2})}{dt} = \sigma\Phi N_{D0} - W_{D10}N_{D1} - W_{A2}N_{A2} - c_{d3}N_{D1}N_{A1} - 2c_{d4}N_{D1}N_{A2} \quad (3.23)$$

Here, $W_{A2} = W_{A21} + W_{A20}$ $W_{A2} = W_{A21} + W_{A20}$ is the total decay rate of acceptor ion in level A2. In our UCNP, the donor doping concentration is roughly one order of magnitude larger than the acceptor concentration. It is therefore reasonable to assume that the excited donor population N_{D1} is also much larger than the excited acceptor population N_{A2} . And the decay rates W_{D10} and W_{A2} have similar value due to substantial quenching by metal[6]. Therefore, the depopulation rate $W_{A2}N_{A2}$ may be considered small compared to the depopulation rate $W_{D10}N_{D1}$. Equation (3.23) can then be simplified to:

$$\frac{dN_{D1}}{dt} = \sigma\Phi N_{D0} - W_{D10}N_{D1} - c_{d3}N_{D1}N_{A1} - 2c_{d4}N_{D1}N_{A2} \quad (3.24)$$

According to the experimental NIR PL rise shown in Fig. 3.6, the population of N_{D1} at the very beginning of the rise process can be expressed by a single exponential

$N_{D1}(t) = N_{D1}^0(1 - e^{-W_{D1}t})$, where N_{D1}^0 and W_{D1} are the steady state population at $t \rightarrow \infty$ and the rise rate of N_{D1} , respectively. Similarly, the population of N_{A1} and N_{A2} can be approximated by single exponential functions: $N_{A1}(t) = N_{A1}^0(1 - e^{-W_{A1}t})$ and $N_{A2}(t) = N_{A2}^0(1 - e^{-W_{A2}t})$. Once again, N_{A1}^0 and N_{A2}^0 are the steady state populations, and W_{A1} and W_{A2} are the rise rates of A1 and A2 levels, respectively. Substituting the expressions of N_{D1} , N_{A1} , and N_{A2} into equation (3.24), and solving for W_{D1} yields,

$$W_{D1} = \sigma\Phi + W_{D10} + 2c_{d4}N_{A2}^0 \left[1 - e^{-W_{A2}t} + e^{(W_{D1}-W_{A2})t} \right] + c_{d3}N_{A1}^0 \left[1 - e^{-W_{A1}t} + e^{(W_{D1}-W_{A1})t} \right] \quad (3.25)$$

For $t \ll \min\{1/W_{A2}, 1/W_{A1}, 1/|W_{D1} - W_{A2}|, 1/|W_{D1} - W_{A1}|\}$, the rate W_{D1} is approximated to

$$W_{D1} = \sigma\Phi + W_{D10} + 2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0 \quad (3.26)$$

The total rise rate W_{D1} can now be determined by fitting the beginning part of the experimentally measured rise in Fig. 3.6 with an exponential function. The results are shown in Fig. 3.8 by blue dash line for nanograting sample, and blue solid line for reference sample. It is clear from equation (3.26) that the total rise rate of transient NIR PL, W_{D1} , three parts: the intrinsic decay rate, W_{D10} , to ground state, the excitation rate $\sigma\Phi$, and the ETU rate, $2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0$. It is straightforward to separate these rates from the total transition rate W_{D1} . Under weak excitation, the excitation rate should be small. Take the excitation power of 1 kW/cm² for example. The excitation rate is only around 12 s⁻¹, which is more than two orders smaller than the total transition rate W_{D1} and intrinsic rate W_{D10} . Also, small excitation rate results in small excited state population and consequently small ETU rate. Thus, the total rise is dominated by W_{D10} .

Fig. 3.6 shows that the rise time under weak excitation is close to 170 μ s for both nanograting

and reference samples. We therefore conclude $W_{D10} = (170 \text{ } \mu\text{s})^{-1} = 5.9 \times 10^3 \text{ s}^{-1}$. With stronger excitation, the excitation rate increases up to around 3700 s^{-1} with the strongest excitation condition (61 kW/cm^2) in our case. Still it contributes less than 20% to the total rise rate W_{D1} . Therefore, the increase of total rise rate under stronger excitation conditions comes from the increased ETU rate, which may be due to the larger population of excited acceptors, N_{A1}^0 and N_{A2}^0 , and also the enhanced energy transfer coefficients, c_{d3} and c_{d4} . When the excitation is strong enough to start depleting the ground state population of acceptor ions, the population N_{A1}^0 and N_{A2}^0 cannot increase further, thus the ETU rate and total rise rate both saturate. This is exactly the trend shown in the transient NIR PL in Fig. 3.6 and Fig. 3.7. And this trend has previously been observed in upconverted luminescence system[7], [86], irrespective of whether plasmonics is involved. However, with the presence of plasmon resonance the total rise and decay rates are higher compared to the case without plasmonics at all excitation conditions. By subtracting the intrinsic rate W_{D10} from the total rise rate W_{D1} , we extract the ETU rate, $2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0$. The largest ETU rates are $1.04 \times 10^4 \text{ s}^{-1}$ and $3.8 \times 10^3 \text{ s}^{-1}$ for nanograting and reference samples, respectively. The plasmonic enhancement of ETU rate is around 2.7 fold. This provides direct evidence that the plasmonic field enhances ETU rate in upconverted luminescence. It is noted that the ETU enhancement factor shown here should not be confused with the PL enhancement factors reported earlier. As discussed in ref [6], the PL enhancement factors depend on the enhancement of absorption and energy transfer coefficient, c_{d4} . Here we discuss the ETU rate, which is a directly measurable quantity defined as the product of energy transfer coefficient and excited state population.

Among the processes governing the population of intermediate energy levels, only the ETU process leads to the desired visible photon emission while the radiative and non-radiative decays both act as loss mechanisms. I define the internal upconversion efficiency as the ratio of ETU rate to total NIR transition rate.

$$\eta = \frac{2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0}{W_{D10} + 2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0} = 1 - \frac{W_{D10}}{W_{D1}} \quad (3.27)$$

The efficiencies are shown in Fig. 3.8 by orange dash line for nanograting sample, and orange solid line for reference sample. The internal upconversion efficiency is close to zero under weak excitation, where decay processes dominate. The efficiency becomes higher under stronger excitation until it reaches the saturation value of 36% for UCNPs on silver film, and 56% for UCNPs on silver nanograting. The presence of plasmon resonance enhances the internal upconversion efficiency by 1.6-fold. Since the internal upconversion efficiency is already high under the strong excitation condition even without the enhancement from plasmonics, the maximum possible enhancement is limited to about 3-fold. Under weak excitation conditions, which correspond to, for example, the solar cell operating condition, much greater enhancement is possible.

The analysis on the decay process can be done similarly. It reveals single exponential decay at the beginning of the NIR decay process, and the decay rate equals to the rise rate obtained from the transient NIR PL rise discussed before. While consistent with the rise analysis, it provides no additional information. Nevertheless, I provide the rate equation analysis of the decay process in the Appendix for completeness.

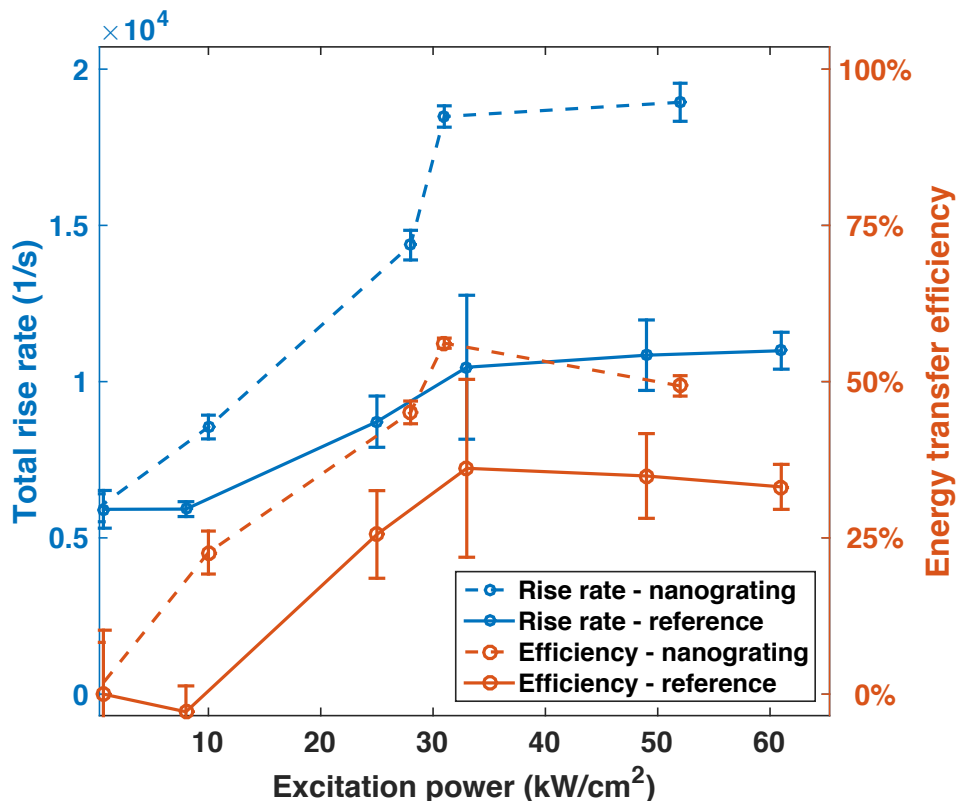


Figure 3.8 The blue curves referring to the left y-axis correspond to the rise rate of UCNPs on silver nanograting (dash line) and on silver film (solid line) respectively for different excitation power densities. The red curves refereeing to the right y-axis correspond to the internal upconversion efficiency of UCNPs on silver nanograting (dash line) and on silver film (solid line) respectively for different excitation power densities.

3.3.2 Transient green emission

The transient green PL depends on three processes: ETU to excite the Er^{3+} ions to the emitting levels, radiative decay from the $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$ levels to ground state $^4\text{I}_{15/2}$ while emitting green photons, and non-radiative decay to intermediate levels and ground state. The total green decay rate, including both the radiative and non-radiative decays, can be directly measured by monitoring the decay of green emission under green laser pulse excitation. I used a 532 nm laser to excite Er^{3+} ions from ground state $^4\text{I}_{15/2}$ level directly into $^2\text{H}_{11/2}$ level, and monitored the

subsequent green emission from Er^{3+} ions in the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels. In this case, the green luminescence exhibits a single exponential decay as shown in Fig. 3.9 (green line) with a decay time of 95 μs .

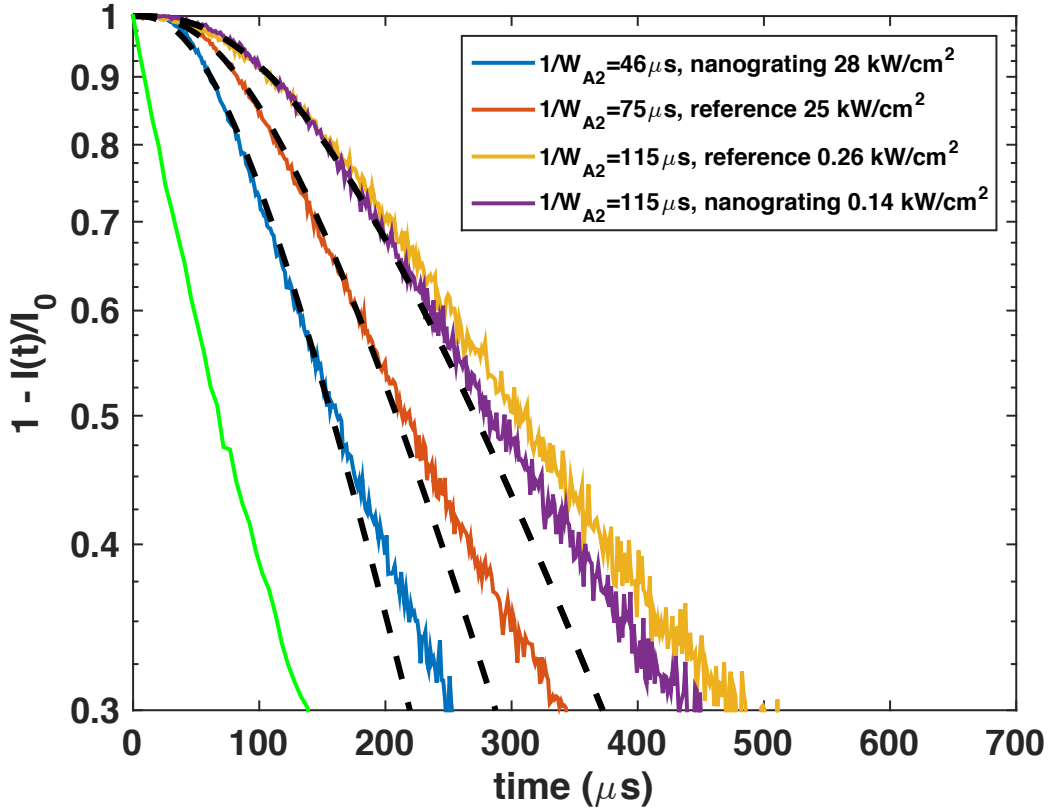


Figure 3.9 Rise of green emission monitored at 550 nm for UCNPs on silver nanograting sample and on reference sample under excitation of a 980 nm laser with different power densities. The rise curves shown in the figure are normalized to steady state green PL intensities, and subtracted by unity, $1 - I(t)/I_0$. The intrinsic green emission decay measured under a 532 nm green laser excitation is shown by the green line with a decay time of 95 μs . The black dash lines are fitting curves based on the analytical solution (Eq. (3.29)).

To investigate the influence of ETU on the transient green emission, I measured the rise of the green emission under 980 nm laser excitation with different excitation conditions as shown in Fig. 3.9. The experimental details are presented in Appendix. Again, the experimentally

measured green PL rise is normalized by the steady state PL intensity, and subtracted from unity so that the rise rates may be extracted. For all excitation conditions, the rise begins slowly because of the competition between ETU and decay. At later times, the rise rate becomes similar to the decay rate (Fig. 3.9, green line). Also, with stronger excitation, the green rise approaches the decay rate, which corresponds to the case of infinitely fast ETU rate. This indicates faster ETU rates under stronger excitation, and is consistent with what we observed in the transient NIR PL. For a similar excitation power density around 25 kW/cm², the rise rate of green emission from nanograting sample is significantly faster than that from the reference sample. It again implies enhanced ETU rate by the plasmon resonance. Under weak excitation, the rise rate of green emission is similar for both samples.

For quantitative study of the green emission dynamics, I perform the rate equation analysis of the transient green emission rise processes. The relevant rate equation for the green emission is equation (3.5), and I re-write here:

$$\frac{dN_{A4}}{dt} = c_{d4} N_{D1} N_{A2} - W_{A4} N_{A4} \quad (3.28)$$

Here, $W_4 = W_{A40} + W_{A43}$ is the total decay rate of green emission. The measured value of W_4 under the excitation by green laser was $(95 \mu s)^{-1} = 1.05 \times 10^4 \text{ s}^{-1}$ as shown in Fig. 3.9. Once again, I approximate the intermediate level population of donor and acceptor ions N_{D1} and N_{A2} with single exponential functions, $N_{D1}(t) = N_{D1}^0 (1 - e^{-W_{D1}t})$ and $N_{A2}(t) = N_{A2}^0 (1 - e^{-W_{A2}t})$. Here, N_{D1}^0 and N_{A2}^0 are the corresponding steady state population at $t \rightarrow \infty$. W_{D1} and W_{A2} are the rise rates of N_{D1} and N_{A2} respectively. Substituting the expression of $N_{D1}(t)$ and $N_{A2}(t)$ into equation (3.28), and solving for normalized green emission population $N_{A4}(t)$ yields,

$$1 - N_{A4} = e^{-W_4 t} - \frac{W_4}{W_4 - W_{D1}} (e^{-W_4 t} - e^{-W_{D1} t}) - \frac{W_4}{W_4 - W_{A2}} (e^{-W_4 t} - e^{-W_{A2} t}) - \frac{W_4}{W_4 - W_{D1} - W_{A2}} (e^{-(W_{D1} + W_{A2}) t} - e^{-W_4 t}) \quad (3.29)$$

In equation (3.29), the green decay rate W_4 and donor NIR transition rate W_{D1} are directly measured from experiments as described previously. By fitting the experimental green emission rise curves in Fig. 3.9 with equation (3.29), I obtain acceptor NIR transition rate W_{A2} as listed in the Table 1 for different excitation conditions. As I increase the excitation power, the acceptor NIR transition rate W_{A2} becomes faster as W_{D1} does. But the ratio of the acceptor transition rate W_{A2} to donor transition rate W_{D1} remains the same at 1.5 for all excitation conditions for both samples, irrespective of the use of plasmonic nanostructure. These results indicate the donor and acceptor transition rates are affected in the same way by the excitation power density and plasmon enhancement, which is not unexpected.

In addition to the study of the transient green emission rise process, I also analyzed the decay process. The calculated NIR transition rate of acceptor ions from decay process is the same as the value I obtained from rise process analysis. As this analysis does not yield any new information, they are provided in the Appendix for completeness.

	Nanograting, 0.14 kW/cm ²	Reference, 0.26 kW/cm ²	Nanograting, 28 kW/cm ²	Reference, 25 kW/cm ²
W_{A2}	$8.70 \times 10^3 \text{ s}^{-1}$	$8.70 \times 10^3 \text{ s}^{-1}$	$2.17 \times 10^4 \text{ s}^{-1}$	$1.33 \times 10^4 \text{ s}^{-1}$
W_{D1}	$5.88 \times 10^3 \text{ s}^{-1}$	$5.88 \times 10^3 \text{ s}^{-1}$	$1.43 \times 10^4 \text{ s}^{-1}$	$8.70 \times 10^3 \text{ s}^{-1}$
W_{A2}/W_{D1}	1.48	1.48	1.52	1.53

Table 3-1 The sample information and excitation conditions are listed in first row. The second row lists the NIR transition rate W_{A2} of acceptor ions fitted from the transient green emission rise curves. The third row

lists the NIR transition rate W_{D1} of donor ions obtained from previous transient NIR emission analysis. The last row lists the ratio of these two rates.

Finally, I discuss possible temperature effects due to the inadvertent heating that may arise from the absorption of light by metal. As commonly observed in luminescent systems[130]-[133], the PL is temperature dependent. Fortunately, the UCNP temperature can be accurately determined by the ratio of two green emission bands ($I_S: {}^4S_{3/2} \rightarrow {}^4I_{15/2}$, $I_H: {}^4H_{11/2} \rightarrow {}^4I_{15/2}$). Due to the close proximity of their energy levels, the two green emission bands arising from the ${}^4S_{3/2}$ and ${}^4H_{11/2}$ levels follow the Boltzmann population distribution[134], [135] [136]

$$I_H / I_S = C \exp(-\Delta E / k_B T)$$

Here, $\Delta E = 600 \text{ cm}^{-1}$ is the energy gap between level ${}^4S_{3/2}$ and ${}^4H_{11/2}$, and C is constant.

The ratio, I_H/I_S , is shown in Appendix for all excitation conditions used in this study, $1 \text{ kW/cm}^2 \sim 61 \text{ kW/cm}^2$. The weakest excitation power density, 1 kW/cm^2 , is deep in the weak excitation regime and it is thus reasonable to assume the temperature of the sample under the weakest excitation is equal to the room temperature[137], 300 K. By converting the intensity ratios into the temperature, I obtain the sample temperatures under all other excitation conditions shown in Appendix. The temperature of the reference sample remains almost the same for the entire excitation power density range while a small increase was observed from the nanograting sample. However, the largest temperature increase in our case was still less than 16 K. Therefore, I believe that the thermal effects under high excitation power density is not important in our study.

3.4 Summary and outlook

The luminescence upconversion system we study here is the most efficient mechanism of ETU where two sensitizer ions (donors) transfer energy to a single activator ion (acceptor) successively to achieve frequency upconversion. The ETU is composed of three distinct physical processes: absorption by sensitizers, successive energy transfer from two sensitizers to an activator, and emission by the activator. Surface plasmon can affect all three processes. When the surface plasmon resonance is tuned to the absorption wavelength, it can enhance both the absorption and energy transfer processes. Absorption enhancement arises from the local field enhancement, which increases the local intensity and consequently absorption. Surface plasmon can also enhance energy transfer process. The exact mechanism of plasmon enhancement of energy transfer process has been disputed. An earlier work attributed it to enhanced local density of states (LDOS)[111]. But more recent works showed LDOS does not influence energy transfer rate[114], [115]. Nevertheless, many theoretical and experimental studies showed plasmon resonance does influence energy transfer rate[6], [72], [121], [138]. This work represents the first experimental demonstration and quantification of plasmon enhanced energy transfer rate in UCNPs. Finally, when plasmon resonance is tuned to the emission wavelength, emission rate can be enhanced via the Purcell effect. I present below a more detailed discussion on each process.

The absorption depends on the local light intensity, absorption cross-section of the active ions and the thickness of the upconversion material. Lanthanide ions generally exhibit small absorption cross-section, due in large part to the forbidden nature of the f-f transitions. Take, for example, $\text{Na}_2\text{Y}_3\text{F}_{11}:\text{18\%Yb}^{3+},\text{2\%Er}^{3+}$ crystal, which is one of the most efficient upconversion materials, an absorption coefficient of 6 cm^{-1} has been reported[70]. For $1\text{ }\mu\text{m}$ thickness sample, only 0.06% of the incident light gets absorbed. An attractive method to improve the absorption

efficiency is to enhance the local field by tuning the plasmon resonance to the absorption frequency[6], [8], [72]. The plasmon mode can generate hot spot near the metal-dielectric interface where upconversion material may be placed. The higher local field naturally leads to more absorption. The absorption enhancement can be directly measured experimentally as we proposed in the steady-state PL study[6]. A simple silver nanograting structure was shown to enhance the absorption by 3 fold. Higher absorption enhancement can be achieved with more sophisticated plasmonic structure design.

For the emission processes, the efficiency is determined by the ratio of radiative decay rate to all other non-radiative decay rates. Ideally, we want to maximize the radiative decay rate and suppress the non-radiative decay rates as much as possible. One major part of the non-radiative decay mechanism is the quenching by defects. By using, for example, core-shell structure[87], [139], the quenching by surface defects can be suppressed. It is also possible to enhance the emission rate by tuning plasmon resonance to the emission frequency[75]. The plasmon mode enhances the local density of photon modes, leading to faster radiative decay rate and higher emission efficiency. The enhancement of the emission rate can be directly visualized from the measurement of PL decay following a pulsed excitation, if sufficiently large enhancement is achieved so that the radiative decay rate exceeds non-radiative rates.

While the understanding of absorption and emission efficiency is relatively straightforward, the energy transfer efficiency has remained difficult to quantify. In the transient PL study, I make a detailed rate equation based analysis, and present a method to experimentally determine the ETU rate and internal upconversion efficiency for various excitation conditions. The internal upconversion efficiency specifies the fraction of rate at which the acceptor ions are excited from the intermediate level to the emitting level. It provides a quantitative metric to

describe the competition between the ETU rate and other loss mechanisms, including the radiative decay of the excited donor and acceptor ions, and the non-radiative energy transfer to metal and defects. Our study reveals that the ETU rate increases with increasing excitation intensity until it reaches saturation, where the highest internal upconversion efficiency is achieved. The highest efficiency is 56% with the enhancement by the plasmonic nanograting, while it remains at 36% for UCNPs in the reference sample. The internal upconversion efficiency and ETU rate are enhanced by 1.6 fold and 2.7 fold, respectively, by the plasmonic nanograting. The 36% internal upconversion efficiency exhibited by the reference sample indicates that the maximum achievable enhancement is about two-fold when operating under strong excitation conditions. Under weak excitation conditions, much greater enhancement should be possible. To our knowledge, we have conducted the first experimental measurement of plasmon enhanced energy transfer upconversion rate and internal upconversion efficiency. Thanks to the enhanced absorption and energy transfer upconversion rate, we have observed up to 16 fold and 39 fold PL enhancement with assistance of plasmonics for green and red emission, respectively. Our work sheds light on how surface plasmon enhances the upconverted luminescence and allows meaningful comparisons among the widely varying reports in the literature. It also offers a firm foundation for more advanced engineering of plasmon-enhanced upconversion materials.

Other than the surface plasmon enhancement I discuss here, there are many other techniques to enhance the efficiency, which is critical in wide applications. The techniques include: core-shell structure for surface quenching passivation[140], [141], annealing process for improved crystallinity[142], donor-acceptor clustering for higher ET efficiency[143], dye-sensitization[144] for broadband absorption and larger absorption coefficients. And more

recently, people have just started the research of long-range energy transfer with metamaterial[145], [146]. It may also have potential application in upconverted luminescence. Many of the techniques described above are compatible with each other. Rarely have people tried to combine different enhancement techniques together in one upconverted luminescence system. I believed that it is promising to improve the efficiency to a new level by doing so. It is also important that people can provide the absolute quantum efficiency, which is absent in almost all literature, so that the comparison of different techniques is possible. With the effort from researchers in different fields, I believe that the efficiency of upconverted luminescence materials can be further improved that could enable even wider applications.

4 Surface plasmon enhanced near field thermal radiation

Thermal radiation has been a topic of great interest over the past centuries. The study of blackbody radiation stimulated the initial development of quantum theory, which opened a new era of human life. The advance of nanotechnology in the past few decades enabled researchers to study thermal radiation in the near field which exhibits many new phenomena, including coherent emission of light by thermal source[147], surface waves excited by thermal source[148], near-field radiation exceeding the blackbody radiation limit[149], [150] and so on. They have a variety of applications, including energy conversion[16], [17], radiative cooling[24], [151], nano-fabrication[152]-[154], and near-field imaging[155]. In this chapter, I will present the study of near-field thermal radiation enhancement by spoof surface plasmon polaritons. I start with thermal radiation in the far-field regime where is governed by the Planck's law. Then, I will give a detailed discussion of near-field electromagnetic local density of states and near-field thermal radiation. After that, I will introduce the spoof surface plasmon polaritons which enable the near-field thermal radiation engineering throughout broad range of frequencies from visible to microwave. In the last, I will discuss the simulation of near-field thermal radiation based on dissipation-fluctuation theorem by the finite-different time-domain (FDTD) method, and compare the results with far-field plane wave excitation modeling.

4.1 Thermal radiation

4.1.1 Far-field thermal radiation

The region that is away from thermal source by several thermal wavelengths $\lambda_T = hc/k_B T$ is defined as the far-field zone or simply the far-field. The thermal radiation in the far-field is governed by the well-know Planck's law. For blackbody, which is an idealized physical body that absorbs all incident electromagnetic radiation irrespective to frequency or incident angle, the thermal radiation intensity in vacuum at thermal equilibrium is

$$I(\nu, T) = \frac{2h\nu^3}{c_0^2} \frac{1}{e^{h\nu/k_B T} - 1} \quad (4.1)$$

where $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ is the Planck constant, ν is the radiation frequency, c_0 is the speed of light in vacuum, $k_B = 1.38 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ is the Boltzmann constant, T is the absolute temperature of the blackbody. The unit of thermal radiation $I(\nu, T)$ is watt per area of emitting surface in normal direction per solid angle per unit frequency. For deeper understanding of the thermal radiation, let us consider a general system at equilibrium temperature T . The electromagnetic energy density $U(\nu)$ at a given positive frequency ν is

$$U(\mathbf{r}, \nu, T) = \rho(\mathbf{r}, \nu) \frac{1}{e^{h\nu/k_B T} - 1} \cdot h\nu \quad (4.2)$$

Here, $\rho(\mathbf{r}, \nu)$ is the electromagnetic local density of states (LDOS), $h\nu$ is the energy of a single photon with frequency ν , $\frac{1}{e^{h\nu/k_B T} - 1}$ is the Bose-Einstein distribution function. It is

straightforward to derive the thermal radiation intensity I in vacuum from the electromagnetic energy density U ,

$$I = \frac{U}{4\pi} \cdot c_0 \quad (4.3)$$

where 4π is the solid angle of a sphere. Substituting the expression of electromagnetic energy density U into Eq. (4.3), we obtain the thermal radiation intensity as

$$I = \rho(\mathbf{r}, \nu) \frac{1}{e^{h\nu/k_B T} - 1} \cdot h\nu \cdot \frac{c_0}{4\pi} \quad (4.4)$$

Recall the LDOS in vacuum is

$$\rho_\nu = \frac{8\pi\nu^2}{c_0^3} \quad (4.5)$$

and one finds that the electromagnetic radiation I in Eq. (4.4) becomes equal to the blackbody radiation in Eq. (4.1). The analysis above provides an intuitive picture of thermal radiation to the electromagnetic energy density and LDOS.

As I stated previously, the blackbody is an idealized physical body. In reality, the thermal radiation from an object is always smaller than or equal to the blackbody thermal radiation in all frequencies. The actual radiation from an object in thermal equilibrium follows the Kirchhoff's law of thermal radiation, which states that: for a body of any arbitrary material, emitting and absorbing thermal electromagnetic radiation at every wavelength in thermodynamic equilibrium, the ratio of its emissive power to its dimensionless coefficient of absorption is equal to a universal function only of radiative wavelength and temperature. That universal function describes the perfect black-body emissive power[156].

4.1.2 Near-field thermal radiation

It is defined as the near-field zone or near-field when one deals with the region within the characteristic thermal wavelength $\lambda_T = hc/k_B T$ from the surface of thermal source. The behavior of thermal radiation may differ dramatically from what it is in the far-field regime due to surface properties especially when there exist surface waves[157].

From the analysis in the previous section, it is clear that the LDOS is critical in thermal radiation. The expression is fairly simple in far-field regime as shown in Eq. (4.5). A more general expression of LDOS in a dielectric environment with refractive index n is

$$\rho_n = \frac{8\pi v^2 n^2}{c_0^3} \quad (4.6)$$

Compared with the relatively simple far-field LDOS, the near field LDOS is much more complicated, and strongly sensitive to local geometry and material properties. It is therefore possible to engineer the local electromagnetic environment to produce near-field LDOS far exceeding the far-field LDOS, leading to many new interesting thermal phenomena.

Let us take a semi-infinite hot metal in vacuum, for example. I have discussed its LDOS in chapter one. For convenience, I re-write the LDOS expression here:

$$\begin{aligned} \rho(z, \omega) = & \frac{\rho_v(\omega)}{2} \left\{ \int_0^1 \frac{\kappa d\kappa}{q} \left\{ 2 + \kappa^2 \left[\text{Re} \left(r_{12}^s e^{i2q\omega z/c} + r_{12}^p e^{i2q\omega z/c} \right) \right] \right\} \right. \\ & \left. + \int_1^\infty \frac{\kappa^3 d\kappa}{|q|} \left[\text{Im} \left(r_{12}^s + r_{12}^p \right) e^{-2|q|\omega z/c} \right] \right\} \end{aligned} \quad (4.7)$$

Here, κ is wave number in unit of ω/c_0 . $q = \sqrt{1 - \kappa^2}$, z is the distance away from the metal surface, ρ_v is the free space LDOS expressed in Eq. (4.5), r_{12}^s and r_{12}^p are the Fresnel reflection

coefficients at the metal-vacuum interface for s and p polarizations, respectively, for a parallel incident wave number $k_{//} = \kappa \omega / c_0$. The LDOS includes the contribution from both electric and magnetic field with s and p polarizations[14]. The first integral for $0 \leq \kappa \leq 1$ corresponds to LDOS contributed by the propagating waves, while the second integral for $\kappa > 1$ corresponds to the contribution from the evanescent waves. In the far-field regime, the contribution from evanescent waves is negligible that the second integral equals to zero. The total LDOS, which is the first integral, equals to the vacuum LDOS ρ_v .

I have mentioned it in chapter one, and want to re-emphasize that the near-field LDOS can exceed the vacuum LDOS ρ_v by over six orders of magnitude at the peak. The corresponding electromagnetic energy density U and thermal radiation is proportionally larger than that in the vacuum. Of course, the majority of the enhancement comes from the evanescent waves. As I have shown in chapter one, the highest LDOS in the near-field regime of a semi-infinite metal occurs at its surface plasmon resonance frequency. Similar LDOS peaks have been observed in SiC and SiO₂ at the corresponding surface phonon polariton resonances[158]. It is desirable to design the LDOS peak at any resonance frequencies we want. Surface plasmon polaritons (SPPs) provides the great flexibility in tuning the resonance frequencies in the visible wavelength regime by nanostructure designs as I have shown in chapter two and chapter three. However, the SPPs is not supported at terahertz (THz) frequencies because metal behaves like perfect electric conductor (PEC). Some nice work[159], [160] has been done to address this issue, and I will discuss it in the next section along with its applications in thermal radiation enhancement.

4.2 Near field thermal radiation enhancement by spoof surface plasmon

4.2.1 Spoof surface plasmon at THz frequencies

As I mentioned in the previous section, the difficulty in tuning surface plasmon polaritons to the THz frequencies is due to the high conductivity of metal in those frequencies. At the metal-dielectric interface, the electromagnetic field is almost excluded from the metal, but extends for many hundreds of wavelengths into the dielectric side[160]. There are no bounded SPPs as we obtained in the visible frequencies. This is also clear from the dispersion relation of SPPs as shown in Fig. 1.4 in chapter one. At low frequency, the dispersion of SPPs approaches the light line. In other words, the SPPs have most of the characteristics of free space light and little of collective electron oscillation in the metal. Therefore, the SPPs are not bounded to the interface (Fig. 4.1(A)). However, by perforating the metal substrate with an array of subwavelength depth holes, bounded surface mode may be supported at the dielectric-metal interface like SPPs in the visible frequency. We will see later that the dispersion relation of this bounded mode is similar to the dispersion relation of SPPs. Therefore it is called spoof surface plasmon polariton (SSPP). The introduce of SSPP enables the ability to engineer the surface wave at almost any frequencies at will[159].

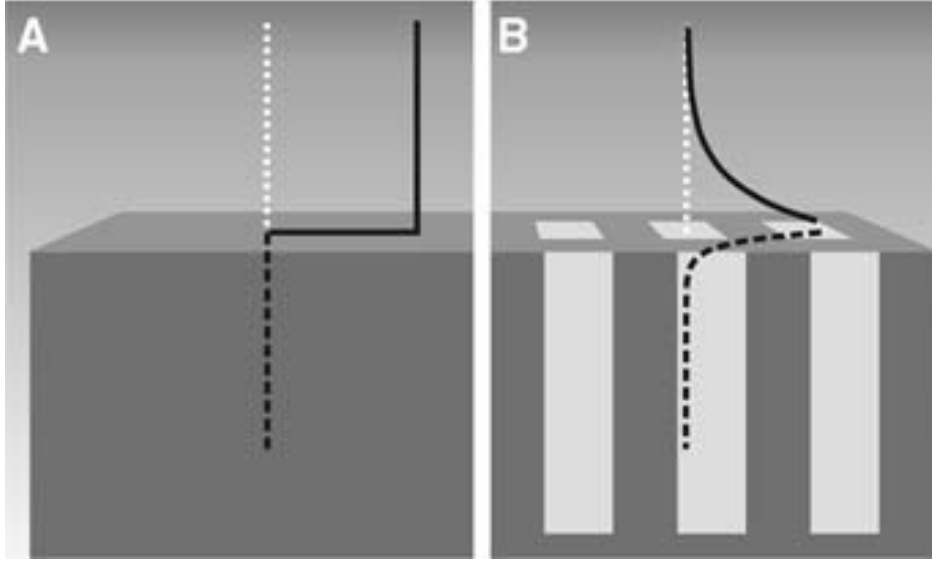


Figure 4.1 Schematic representation of electric field at the interface of metal-dielectric at THz frequency. (A) The metal is almost perfectly conducting that the electric field is almost completely excluded from it. On the side of dielectric, the electric field extends for many hundreds of wavelengths. (B) Metal substrate perforated with subwavelength depth holes supports the exponentially decay electric field in the metal side and dielectric side. The bounded surface mode is known as spoof surface plasmon polariton. (Ref [160]).

Analysis of metal substrate perforated with one-dimensional array of grooves and two-dimensional array of holes that support SSPP can be found in reference [159], [161]. Here, let us analyze the structure of one-dimensional array of grooves for deeper understanding of SSPP. The structure is shown in Fig. 4.2 where the metal is treated as perfect electric conductor, which is a good approximation of metal at the THz frequencies. The whole structure is in vacuum. For simplified analysis, let us only consider the case that $\lambda_0 \gg d$ and $\lambda_0 \gg a$, where λ_0 is the free space wavelength, d and a are the periodicity and aperture size of the groove array.

Let us consider the TM incident wave with wave number k_x in x direction, and searching for the bounded surface modes. The electromagnetic fields are

$$\begin{aligned}
\vec{E}^{inc} &= \frac{1}{\sqrt{d}} e^{ik_x x} e^{ik_z z} \begin{pmatrix} 1 \\ 0 \\ -k_x/k_z \end{pmatrix} \\
\vec{H}^{inc} &= \frac{1}{\sqrt{d}} e^{ik_x x} e^{ik_z z} \begin{pmatrix} 0 \\ k_0/k_z \\ 0 \end{pmatrix}
\end{aligned} \tag{4.8}$$

where $k_0 = \omega/c_0$ is the wave number, and $k_z = \sqrt{k_0^2 - k_x^2}$ is the wave number in z direction. The reflected electromagnetic waves for the n^{th} diffraction order are

$$\begin{aligned}
\vec{E}^{ref,n} &= \frac{1}{\sqrt{d}} e^{ik_{x,n} x} e^{-ik_{z,n} z} \begin{pmatrix} 1 \\ 0 \\ k_{x,n}/k_{z,n} \end{pmatrix} \\
\vec{H}^{ref,n} &= \frac{1}{\sqrt{d}} e^{ik_{x,n} x} e^{-ik_{z,n} z} \begin{pmatrix} 0 \\ -k_0/k_{z,n} \\ 0 \end{pmatrix}
\end{aligned} \tag{4.9}$$

where $k_{x,n} = k_x + 2\pi n/d$ with integer n from $-\infty$ to $+\infty$, and $k_{z,n} = \sqrt{k_0^2 - k_{x,n}^2}$. The total electromagnetic fields in region I is given by the summation of incident and reflected fields:

$$\begin{aligned}
\vec{E}^I &= \vec{E}^{inc} + \sum_{n=-\infty}^{\infty} \rho_n \vec{E}^{ref,n} \\
\vec{H}^I &= \vec{H}^{inc} + \sum_{n=-\infty}^{\infty} \rho_n \vec{H}^{ref,n}
\end{aligned} \tag{4.10}$$

where ρ_n is the reflection coefficient associated with the diffraction order n. The reflection coefficient ρ_n can be extracted from the boundary conditions:

$$\rho_n = - \frac{2i \tan(k_0 h) S_0 S_n k_0/k_z}{1 - i \tan(k_0 h) \sum_{n=-\infty}^{\infty} S_n^2 k_0/k_{z,n}} \tag{4.11}$$

where h is the depth of the groove, and S_n is the overlap integral between the n^{th} plane wave and the fundamental TE mode. It equals to

$$S_n = \sqrt{\frac{a}{d}} \text{sinc}\left(k_{x,n} a/2\right) \quad (4.12)$$

We can obtain the dispersion relation of the bounded surface mode by calculating the poles of the reflection coefficients Eq. (4.11):

$$\frac{\sqrt{k_x^2 - k_0^2}}{k_0} = S_0^2 \tan(k_0 h) \quad (4.13)$$

For $k_x a \ll 1$, the dispersion relation simplifies to

$$\frac{\sqrt{k_x^2 - k_0^2}}{k_0} = \frac{a}{d} \tan(k_0 h) \quad (4.14)$$

For the case $a/d = 0.2$ and $h = d$, the dispersion relation is shown in Fig. 4.3 following the Eq. (4.14). Compared with the dispersion relation of SPPs, the dispersion relation of this bounded surface mode in THz frequency shares lots of similarities. For largest k_x , the angular frequency ω approaches $\omega_{\text{spoof}} = \pi c_0 / 2h$ which is the frequency of the fundamental cavity waveguide mode inside the groove in the limit of $a/d \rightarrow 0$. This is analogous to the surface plasmon frequency ω_{sp} of SPP discussed in chapter one. For this reason, this bounded surface mode is called spoof surface plasmon polariton (SSPP).

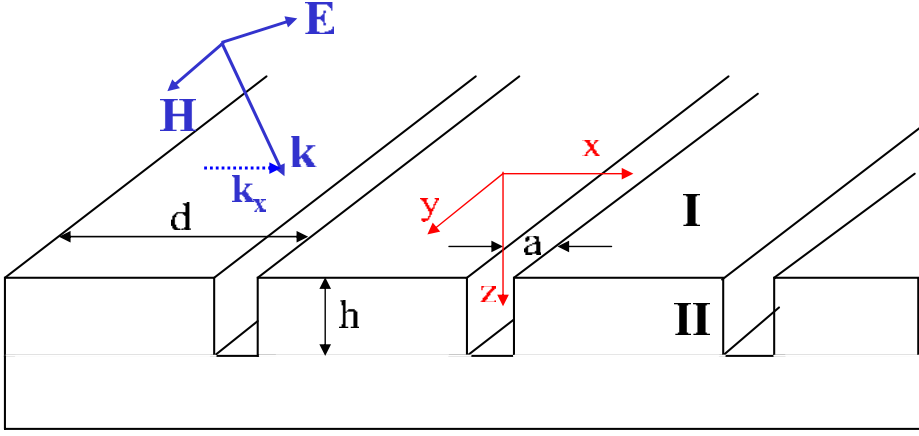


Figure 4.2 The metal substrate (region II, treated as perfect electric conductor) perforated by one-dimensional array of grooves for the study of SSPP. The periodicity of the array is d with groove depth of h and aperture size of a . The whole metal structure is in vacuum (region I). The incident electromagnetic field is represented in blue arrows. The coordinates are in red arrows. The incident wave number in x direction is k_x . (Ref [161])

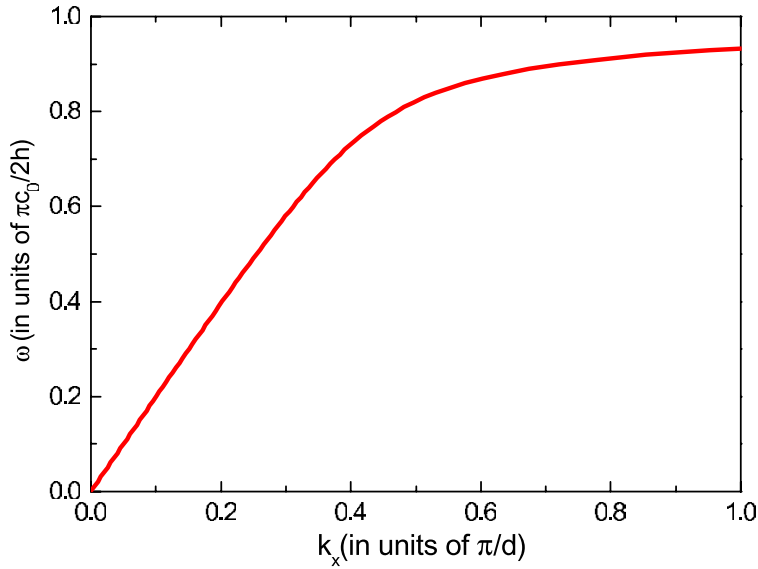


Figure 4.3 Dispersion relation (Eq. (4.14)) of the bounded surface mode supported by one-dimensional array of grooves (structure shown in Fig. 4.2). The structural parameters are $a/d=0.2$ and $h=d$. (Ref [161])

4.2.2 Far-field excitation of spoof surface plasmon polariton

In the previous analysis, the dispersion relation Eq. (4.14) is the approximation under conditions:

$\lambda_0 \gg d$, $\lambda \gg a$ and $k_x a \ll 1$. Exact solution of the dispersion relation and the SSPP field profile can be obtained from simulation. Here I use finite-difference time-domain (FDTD) method to design a one-dimensional structure that supports SSPP at 5 THz, which is of special interest for rectenna operation[162]-[164]. I will explore the SSPP mode profile and field enhancement. In addition, I add a bow-tie antenna in the near-field to further enhance the electromagnetic field and concentrate near-field energy to the antenna feed point.

The structure I designed is copper substrate perforated by one-dimensional grooves shown in Fig. 4.4(c). The substrate is coated by a 1 μm thick SU-8 film as an electrical and thermal insulation layer. The background dielectric medium is air. The periodicity of the grooves is 24 μm with groove depth of 7.3 μm and aperture size of 2 μm . Considering the presence of SU-8 with refractive index of 1.7, the theoretical SSPP resonance frequency calculated from Eq. (4.14) should be around 6 THz. While the simulation shows reflectance resonance at 5 THz as shown in Fig. 4.4(a) under excitation of far-field transvers magnetic (TM) polarized plane wave. The discrepancy arises from the fact that I use the Drude dielectric function[1] for copper substrate instead of PEC assumed in deriving Eq. (4.14). Also, the feature sizes do not well satisfy the approximations made in the analytical study.

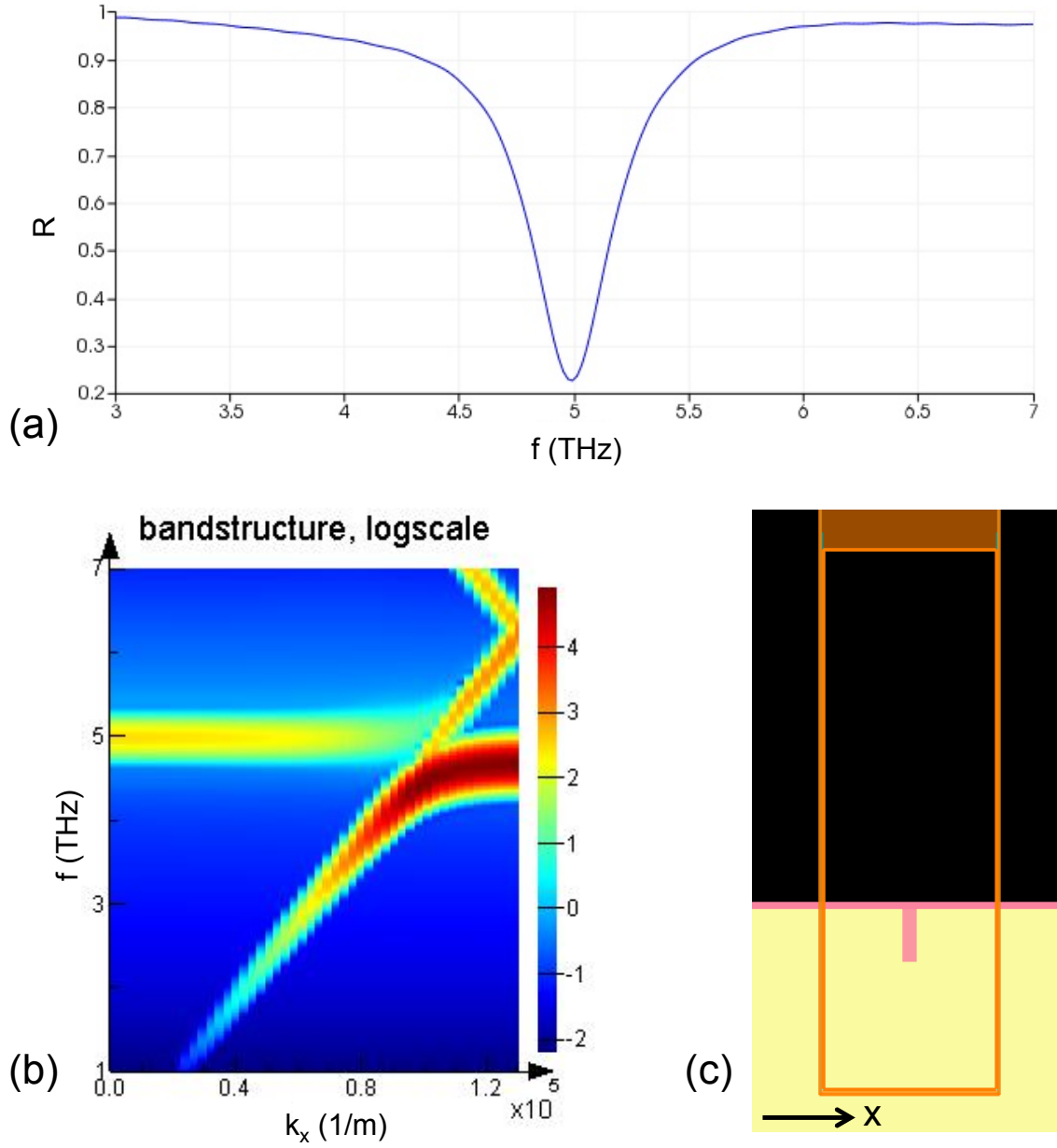


Figure 4.4 (a) The reflectance spectrum of the perforated copper structure (c) with one-dimensional array of grooves under far-field plane wave excitation with TM polarization and normal incident angle. (b) The bandstructure under logarithmic color scale. The color bar corresponds to the relative mode magnitude. k_x is the mode wave number in the x direction (orthogonal to the alignment of grooves). (c) The computational unit marked by orange box with periodic boundary condition on x direction (denoted by arrow). One micrometer thick SU-8 is coated on the copper substrate and fills the grooves. Copper is in yellow, SU-8 is in red, and vacuum is in black. Structural parameters are stated in the text.

To further confirm the mode at the reflectance spectrum resonance, I calculate the bandstructure using FDTD method. The result is shown in Fig. 4.4(b). k_x is the wave number in the direction orthogonal to the alignment of grooves (x-direction marked in Fig. 4.4(c)). The maximum value of k_x is set to the first Brillouin zone π/Λ , where $\Lambda = 24 \mu\text{m}$ is the periodicity. The straight line, which bounces back at the Brillouin zone boundary, is the light line. The dispersion curve that bends around 5 THz is the SSPP we are looking for. The overall trend of the dispersion curve is consistent with the theoretical dispersion relation of SSPP (Fig. 4.3). It overlaps with the light line at low frequency, and bends to the right side at higher frequency. Close to the SSPP resonance frequency, the dispersion curve is almost flat which indicates close to zero group velocity. The mode thus acquires electrostatic character[165] which obeys the solution of Laplace equation for time independent electromagnetic fields. All these properties mimic the surface plasmon polaritons in the visible frequency discussed in chapter one. Therefore, I verify that the reflectance spectrum resonance at 5 THz comes from the coupling of incident plane wave to SSPP.

The flat dispersion curve at SSPP resonance frequency corresponds to large LDOS, thus large electromagnetic field and energy density. It is of our interest to see how large an enhancement the SSPP can achieve compared with the incident field and with the case of surface plasmon polaritons. Fig. 4.5 shows the mode profile at resonance frequency of 5 THz. The largest electric field enhancement can reach 20-fold at the interface of metal and dielectric (SU-8 in this case). The field resides mostly inside the groove etched on the metal substrate as sketched in Fig. 4.1(b). And it decays away from the metal-dielectric interface. On the top surface of SU-8 (1 μm above the metal surface), the field enhancement can still reach 8-fold, which corresponds to 64-fold energy density enhancement. This validates our idea of using SSPP resonance to

achieve near-field energy enhancement. It is worth noting that the actual field enhancement strongly depends on the specific design of structure as we have observed in the case of SPPs[8], [45], [166]. The field enhancement we observe here by SSPP is comparable with that from the SPP cases. Since the feature sizes of the structure are much smaller than the free space wavelength of interest, we name the structure a metamaterial.

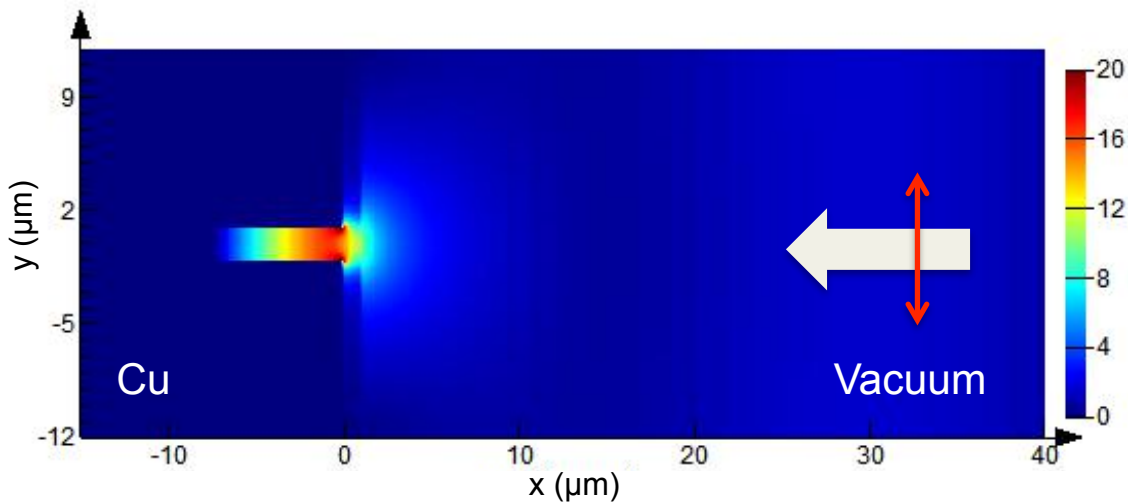


Figure 4.5 The electric field profile at resonance frequency of 5 THz. The structure is shown in Fig. 4.4(c). The incident plane wave (white arrow) is polarized in y direction marked by red arrow. The color bar in linear color scale represents the electric field magnitude normalized to the magnitude of incident field. It is actually the field enhancement.

I move one-step further to integrate the bow-tie antenna in the near-field of the metamaterial for even higher field enhancement and energy concentration for the application of energy conversion by rectenna[164], [167]. I put two-dimensional array of bow-tie antennas on top of SU-8 surface as shown in Fig. 4.6(a). The antenna is made of gold with thickness of 1 μm , and single arm length of 4 μm . The angle of the bow-tie is 30-degree with square feeding area of 800 nm by 800 nm between the two antenna arms. The periodicity of antenna array is the same as the grooves $\Lambda = 24 \mu\text{m}$. I use the Drude model for the dielectric function of gold[1]. The

simulated reflectance spectrum (Fig. 6(b)) exhibits strong resonance close to 5 THz. It is the resonance frequency of SSPP supported by the metamaterial. I designed the antenna parameters so that its presence does not change the resonance frequency of the metamaterial, while the interaction of antenna and the metamaterial can further enhance the field intensity. The electric field profile on the x-z plane cut through the center of bow-tie antenna is shown in Fig. 4.6(c). We can still observe the SSPP near the metamaterial surface with similar intensity as the case without antenna (Fig. 4.5). Instead of having the largest field near the metal-dielectric interface, the presence of antenna shifts the field maximum to the antenna feed-point located between the two arms. Compared with the incident field, the largest enhancement near the antenna boundary is over 35-fold due to both the surface plasmon and the lightning rod effect. Away from the antenna edge, the field in the antenna gap is quite uniform with slightly smaller enhancement around 30-fold. Recall the enhancement factor of 8-fold 1 μm away from the metamaterial where the antenna resides, the antenna contributes additional 4-fold enhancement of the electric field. For better understanding of the field profile around the antenna feeding area, I also examined the field in the x-y plane through the center of the bow-tie antenna. The field profile is shown in Fig. 4.6(d), which is again normalized to incident field magnitude. Similar enhancement is observed. It validates our conclusions drawn from the analysis of x-z cross plane on field enhancement. With the antenna structure integrated on top of metamaterial, the energy density enhancement (square of the electric field enhancement) in the antenna gap region is around 10^3 fold. With more sophisticated metamaterial design, it may be possible to obtain even higher enhancement which can be extremely useful in the applications, e.g. energy conversion.

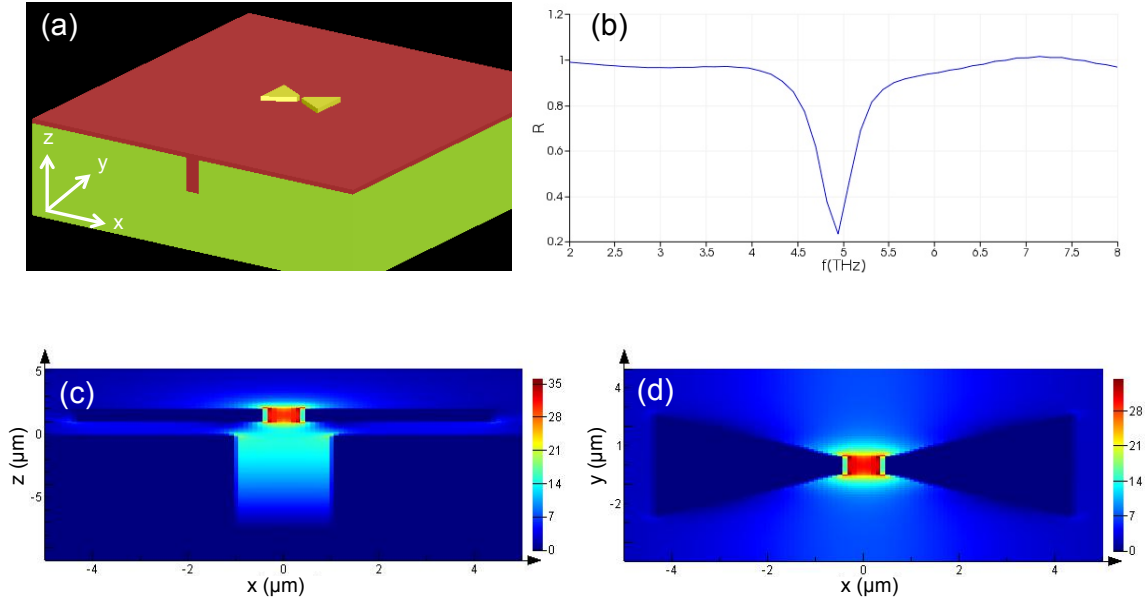


Figure 4.6 (a) Two-dimensional array of bow-tie antennas (in gold) integrated on top of SU-8 (in red) with the gold substrate (in green) perforated with one-dimensional array of grooves. The white arrows show the coordinate. (b) Reflectance spectrum of the whole structure with plane wave incidence polarized orthogonal to the groove alignment. (c) Electric field magnitude on x-z plane cut through the center of the bow-tie antenna. The color bar is the field magnitude normalized to incident field. (d) Electric field magnitude on x-y plane cut through the center of bow-tie antenna. Again, the color bar is the field magnitude normalized to incident field. Note that (c) and (d) do not show the whole single unit cell, but zoom in the antenna area.

4.2.3 Near-field thermal radiation modeling

All the studies discussed previously are based on far-field plane wave excitation. However, some of the major applications, especially the thermal energy conversion, operate under thermal excitation of the metamaterial surface. The physical properties of these two types of excitation sources are fundamentally different in many ways, especially the temporal and spatial coherence. There are abundant studies of far-field excitation coupling into near-field surface waves[2], [5], [168]. Rarely have people studied the coupling of near-field thermal source into surface waves[147], [148], especially in the near-field regime due to the difficulties in both experiments and modeling, though it is important in thermal energy conversion applications. In this section, I will first introduce the thermal excitation modeling based on dissipation-fluctuation theorem by the FDTD method. Then, I will validate the modeling method by comparison with analytical solutions for single metal-dielectric interface. In the next section, I will study the excitation of SSPP by thermal source, and the enhanced near-field thermal radiation.

A few methods are applicable to model thermal radiation[169]: partial wave scattering method, boundary element method, and FDTD method. Among them, FDTD method is the most versatile, because it can deal with arbitrary geometry and various types of dispersive materials. I will describe how the FDTD method can be used to model the thermal electromagnetic radiation by incorporating the Langevin approach to Brownian motion[170], [171].

In the presence of thermal excitation, the polarization response $\mathbf{P}$ of the material to local electric field $\mathbf{E}$ can be described by

$$\frac{d^2\mathbf{P}}{dt^2} + \gamma \frac{d\mathbf{P}}{dt} + \omega_0^2 \mathbf{P} = \sigma \mathbf{E} + \mathbf{K}(t) \quad (4.15)$$

where γ is the damping parameter of the polarization system, ω_0 , σ is the resonance frequency and strength, respectively. The force from random thermal fluctuation is represented by the term

$\mathbf{K}(t)$, which adds the perturbation to the polarization response. It is implemented in FDTD method by adding one random term $\mathbf{K}(t)$ to polarization $\mathbf{P}$ after each simulation time step. Based on fluctuation-dissipation theorem[172], the time correlation of $\mathbf{K}(t)$ can be expressed in frequency domain by

$$\overline{K_\alpha(\mathbf{r}, \omega) K_\beta^*(\mathbf{r}', \omega)} = \frac{4}{\pi} \sigma \gamma I(\omega, T) \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') \quad (4.16)$$

where $I(\omega, T)$ represents the free space Planck blackbody radiation intensity, $K_{\alpha,\beta}$ are the components of K , the bar on the left side of Eq. (4.16) is the correlation operator which is

$$\overline{K(\mathbf{r}) K^*(\mathbf{r}')} = \lim_{r_0 \rightarrow \infty} \int_{-r_0/2}^{r_0/2} K[\mathbf{r}' + (\mathbf{r} - \mathbf{r}')] K^*(\mathbf{r}') d\mathbf{r}'$$

The frequency dependence of the correlation makes the generation of $\mathbf{K}(t)$ computationally expensive. Taking the advantage of electromagnetism linearity in a linear material[173], we can use a random white noise source $\mathbf{K}'(\mathbf{r}, \omega)$ instead. The correlation function becomes

$$\overline{K'_\alpha(\mathbf{r}, \omega) K'^*_\beta(\mathbf{r}', \omega')} = \frac{4}{\pi \Delta V} \sigma \gamma \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') \delta_{\omega\omega'} \quad (4.17)$$

The simulated thermal radiation spectrum or any quantity proportional to the squared Fourier amplitudes is normalized to $I(\omega, T)$ with a constant calibration factor. In the time domain, the discretized random white noise $K'(\mathbf{r}, \omega)$ is correlated as

$$\overline{K'_\alpha(\mathbf{r}, t) K'^*_\beta(\mathbf{r}', t')} = \frac{4}{\pi N \Delta V} \sigma \gamma \delta_{\alpha\beta} \delta_{rr'} \delta_{tt'} \quad (4.18)$$

where N is the number of time steps in the FDTD simulation, and ΔV is the mesh element volume. To simplify the generation of $\mathbf{K}'(t)$, we can choose a uniform distribution over the range $\pm(12\sigma\gamma/\pi N\Delta V)^{1/2}$ [169].

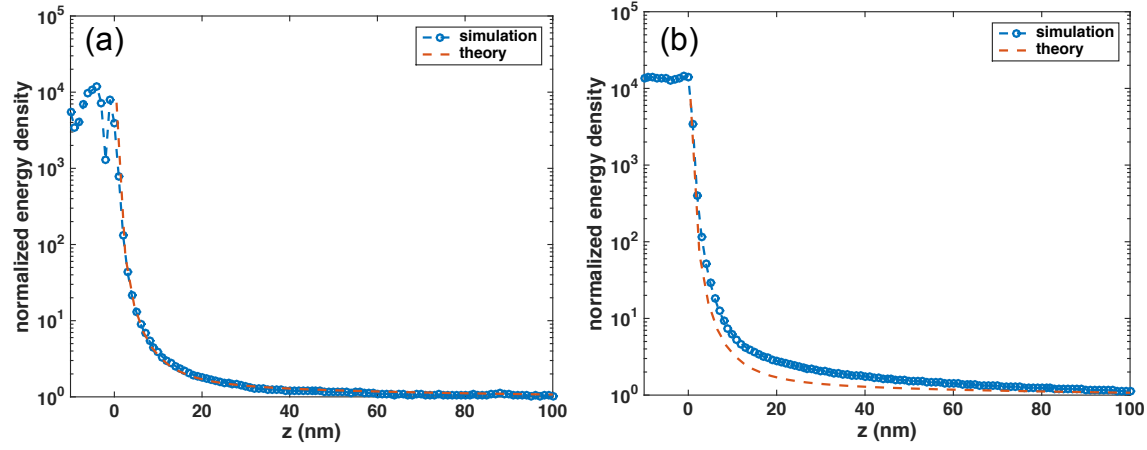


Figure 4.7 The normalized electromagnetic energy density in the vicinity of aluminum surface (vacuum: $z > 0$, aluminum: $z < 0$) at wavelength of 500 nm. The values are normalized to free space energy density. Results from simulations are denoted by blue dots. Theoretical values are in red dash lines. (a) is monitored near the center of computational domain. (b) is the averaged result over the whole computational domain. Both (a) and (b) use logarithmic scale in y axis.

The thermal modeling based on FDTD method is well established, and widely used[169]-[171]. In most of the literatures, the thermal modeling is implemented with their own in-house FDTD algorithm. Here, I incorporate the thermal modeling with commercial FDTD software (Lumerical FDTD) which has easy access. The idea is to add a random perturbation to the polarization at each FDTD time step using the software tool “flexible material plugins”. In order to validate our model, I compare the simulation results with theoretical values. The structure I simulate is a hot semi-infinite aluminum put in free space (vacuum). I want to calculate the electromagnetic energy density from the simulation, and compare with analytical solution given in Eq. (4.2) and Eq. (4.7). Again, I use the Drude model for aluminum dielectric function[174].

The computational domain consists only of a thick aluminum in the lower half backed by perfect matching layer (PML), and air in the upper half backed by PML as well. In the simulation, I use unit cell size of 1 μm with periodic boundary condition to represent the infinite aluminum surface. Limited by the computational resources, I choose the uniform mesh size of 1 nm. The electromagnetic energy density extracted from the thermal simulation is normalized to the free space energy density, and shown by blue dots in Fig. 4.7. The energy density monitored close to the center of the computational domain is shown in Fig. 4.7(a), which exhibits excellent matching to analytical values (red dash line). Due to the nature of thermal fluctuation, the energy density varies over the plane that has a fixed distance away from the aluminum surface. To minimize the fluctuation effect for more rational comparison with theoretical values, I average the energy density for different distances over the whole computational domain, and show the results in Fig. 4.7(b). It is exciting to observe the largely enhanced energy density in the near-field regime, especially below the distance of 20 nm to the aluminum surface where the energy density increases dramatically by almost four orders. The quick change of energy density over the small spatial dimension requires sufficiently small mesh size, which can be one of the reasons for the small discrepancy of simulation results and theoretical values. The huge energy density in the near field is due to the contribution from evanescent waves as I discussed previously, and the harvesting of the huge near-field energy attracts lots of attention.

4.2.4 Near-field thermal radiation enhancement by spoof surface plasmon

People have observed the evidences of thermal source coupling to surface waves, resulting in the coherent emission[147], [148], and near-field radiative heat transfer exceeding blackbody radiation[25], [26]. However, the surface modes studied in literature are mostly surface phonon polaritons and surface plasmon polaritons, which have the limitation in resonance frequency

tuning. Here, I study the thermal excitation of SSPP that enables the design of resonance frequency in almost all frequencies [159], especially in the THz frequencies where thermal energy conversion by rectenna [162], [164] is feasible.

The structure I study here is exactly the same as that used in the far-field excitation section (Fig. 4.5(c)). It is one-dimensional array of grooves in copper substrate coated with SU-8 insulation layer. The difference is the excitation source. Instead of far-field TM polarized plane wave, the source here is thermal excitation represented by the polarization fluctuation within the copper substrate. The simulation runs over 5000 femtoseconds to reach steady state, and is post processed to temperature 800 K by matching the far-field thermal radiation with Kirchhoff's law. The simulated electric field profile is normalized to the far-field thermal radiation, which is close to the blackbody radiation due to the large absorptivity as shown in Fig. 4.4(a). The field profile is shown in Fig. 8 at the frequency of 5 THz, where the SSPP resonance is for this structure based on the bandstructure analysis (Fig. 4.4(b)). Compared with the SSPP in Fig. 4.5, the thermally excited mode exhibits the same features. The mode is bounded to the metal-dielectric interface around the grooves as expected for the SSPP. The highest field resides at the interface of the grooves and the flat dielectric film, and decays both ways. Therefore, it is reasonable to believe that the mode we observe here under thermal excitation is the SSPP. The maximum field enhancement is around 10-fold, which is half of what we observed in far-field excitation case (Fig. 5). It indicates less efficient coupling from thermal source to the SSPP. It is reasonable considering that the radiation from the thermal source is randomly polarized while the far-field plane wave is TM polarized which has the best coupling efficiency. You may have noticed that there is no explicit source in the whole computational domain. The energy that drives the system

all comes from the random fluctuation of polarization in the copper substrate, and the electric field there is highly non-uniform (Fig. 4.8) as expected.

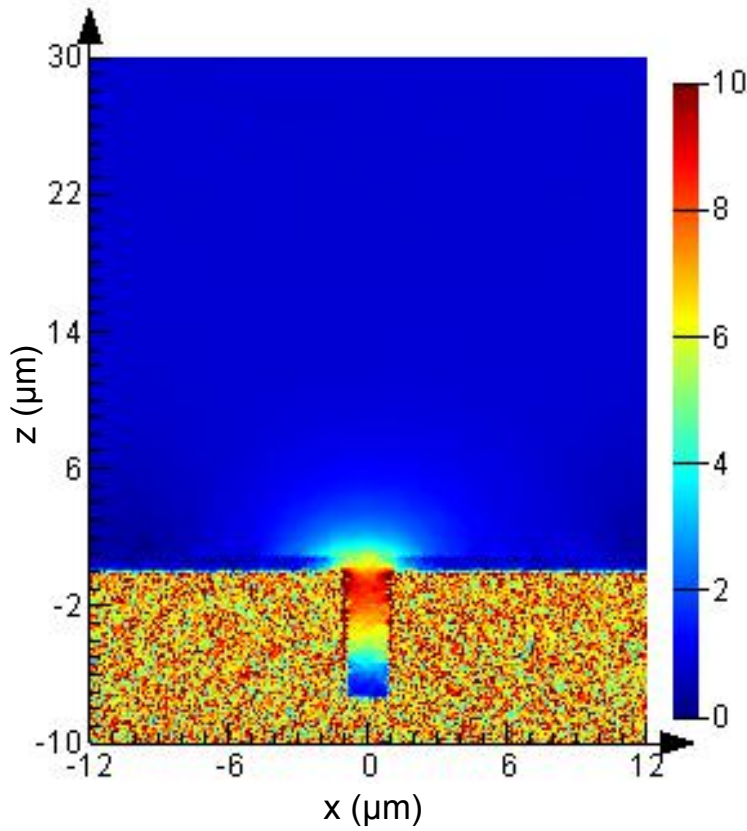


Figure 4.8 Electric field normalized to far-field thermal radiation at resonance frequency of 5 THz. The color bar represents the normalized magnitude. The thick copper substrate is on the bottom serving as the thermal source. One micrometer thick SU-8 is coated on top of copper, and fills the grooves. The whole structure is periodic in x direction, and exposed to air (vacuum). Only one unit cell is shown in this figure.

To my best knowledge, this is the first observation of thermally excited spoof surface plasmon polariton that provides near-field energy density hundred times higher than the free space blackbody radiation.

For even higher energy density enhancement over desired area, I design two-dimensional array of bow-tie antennas on top of the SU-8 insulation layer. The structure is exactly the same

as shown previously in Fig. 4.6. From the normalized electric field in Fig. 4.9, we can still see the SSPP profile though much weaker than the maximum field concentrated at the gap between the two antenna arms. The field profiles over both the x-z cross plane (Fig. 4.9(a)) and x-y cross plane (Fig. 4.9 (b)) look similar to the case under far-field plane wave excitation (Fig. 4.6(c) & (d)). In the antenna gap, the electric field is uniformly enhanced by around 20 fold. Compared with the enhancement factor of around 5 fold at one micrometer above the copper substrate where the antenna locates, the antenna provides additional enhancement of electric field around 4 fold. This is consistent with our analysis in the far-field excitation case. The final enhancement of energy density reaches 400 fold over the blackbody radiation.

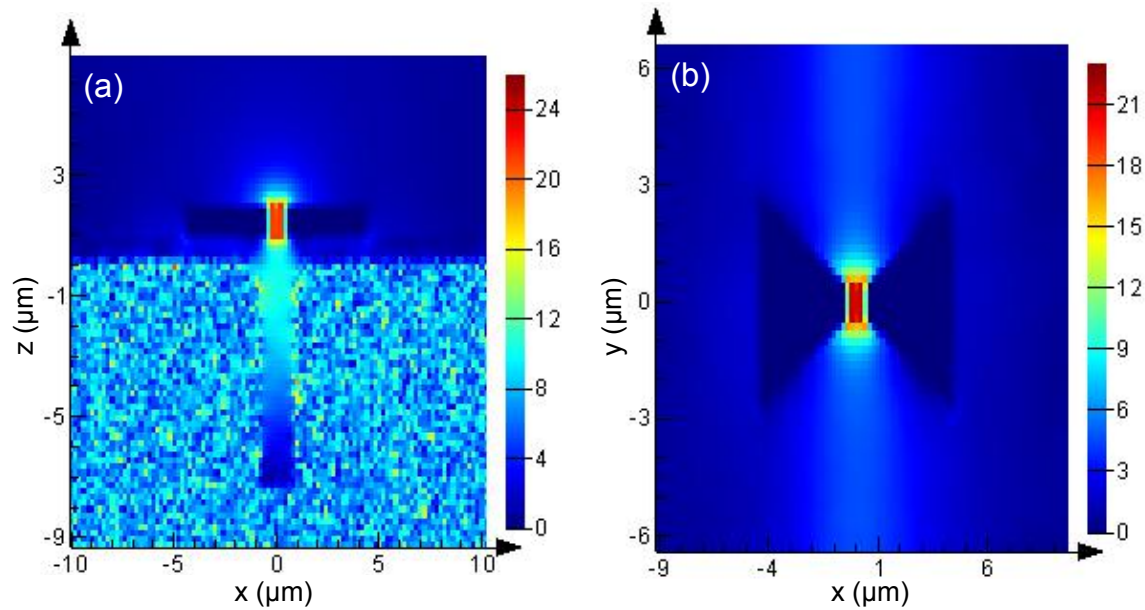


Figure 4.9 Electric field normalized to the far-field amplitude at frequency of 5 THz. (a) The x-z plane cross the center of bow-tie antenna in y direction. (b) The x-y plane cross the center of the antenna in z direction. The color bars represents the field magnitude.

4.3 Summary and outlook

This chapter focuses on the enhancement of near-field thermal radiation exceeding the blackbody radiation through evanescent surface waves. As we know, the energy density is linearly proportional to the LDOS. In the far-field regime, the LDOS is contributed by the propagating waves where the energy is stored in. While in the near-field regime, the major contribution to LDOS comes from the evanescent surface waves, e.g. surface plasmon polaritons, surface phonon polaritons, and SSPP. By exciting these surface waves, the total LDOS can far exceed the free space LDOS. In chapter one, I have calculated the LDOS close to the gold-air interface. The near-field LDOS can be over six orders of magnitude larger than the free space LDOS, thus the energy density by the same amount. This could be especially useful in the applications, such as thermal energy conversion, and radiative heating. Lots of research has been reported for the engineering of near-field radiation. However, most of them are based on the study of far-field plane wave excitation[167], [168], instead of actual thermal excitation. And the surface waves mostly studied are surface phonon polaritons which are difficult to tune the resonance frequency. Some research studies the surface plasmon polaritons whose resonance frequency only has tenability in the visible frequency range. Here, I focus on the spoof surface plasmon polariton supported by simple periodic structure (one-dimensional array of grooves) on metal substrate (gold, copper, silver and so on). The resonance frequency can be tuned almost anywhere desired. I intentionally tune the resonance frequency to 5 THz for the sake of rectenna operation for potential application in thermal energy conversion. The structural design is implemented with the model of far-field plane wave excitation. And the bandstructure calculation verifies the SSPP resonance at 5 THz. Then, I apply the same structure for the thermal modeling. The thermal excitation is based on the FDTD method by incorporating the Langevin approach to Brownian

motion. It excites the same SSPP mode at same frequency as we observed in far-field plane wave excitation model. To our best knowledge, this is the first report of thermally excited SSPP. The near-field radiation is enhanced by 400-fold exceeding the blackbody radiation. With more sophisticated structural design, I believe that higher near-field radiation enhancement is achievable.

The near-field radiation is attracting more attentions thanks to its applications and interesting physics behind it. People have studied the spatial coherence of electromagnetic wave emission from thermal source, while the exploration of temporal coherence is still rare[175]. Traditionally, the thermal radiation is treated as an example of incoherent source in contrast to laser. It has broadband in frequency domain which corresponds to poor temporal coherence. With the coupling to coherent surface waves can dramatically improve the temporal coherence, which may have potential impact on the energy conversion. Other interesting topics include thermal switching[176], radiative cooling[151] and high temperature metamaterial for thermal emission control[177]. With easy access to the thermal modeling tool we developed with commercial software, the future of thermal radiation research looks brighter than ever.

5 Summary

The phenomena of surface plasmon have been observed over a century ago in the Wood's anomalies[165]. Thanks to the advance of nanotechnology during the past few decades, the research of surface plasmon gains great momentum, spawning a variety of interesting topics including bio-sensing[178], medical therapy[179], nanofabrication[154], super-resolution imaging[12], data storage[9], SERS[180], and so on. Among all these exciting topics, the application of surface plasmon to energy technology[5], [149], [181], [182] attracts our special interest for its significance and impact on the society with increasing demand of clean energy.

First, I present my research on the application of surface plasmon to semiconductor photovoltaic (PV) devices in chapter two. The inability of utilizing low energy photons from solar radiation limits the efficiency of traditional semiconductor PV devices. It is a general problem in semiconductor PV devices arising from the bandgap of semiconductor materials. Photons with energy smaller than the bandgap pass through the semiconductor active layer with little absorption. One idea to extend the absorption band[5] is to enhance the local field so that the absorptivity can be greatly improved from the initial small absorption coefficient. This is especially useful near the band edge where the absorption coefficient is not too small that a decent enhancement of local field can result in appreciable absorptivity. As for the local field enhancement, surface plasmon has a reputation in achieving large field enhancement[183]. I apply this idea to organic photovoltaic (OPV) device with active layer of semiconductor polymer PCDTBT: PCBM[5]. With minimal changes to the traditional OPV device, I patterned the back electrode with one-dimensional grating structure that supports surface plasmon resonance at the band edge of OPV active layer. The overall absorption enhancement reaches around 10%

compared to the device without patterned back-electrode. Further study reveals that there are actually two surface plasmon modes in the device: surface plasmon polaritons and localized surface plasmon polaritons. The observation of multiple modes in plasmon enhanced OPV devices is common[5], [43], [44], [47], [184], [185], while the detailed study of the interaction between multiple modes is usually omitted. I conducted systematical study, and reveal that the two modes interact strongly with each other showing anti-crossing behavior. The field profile in the absorbing active layer also changes due to the mode interaction which eventually affects the overall absorption of OPV devices. My work shows that the full optimization of plasmon enhanced OPV design must take into account the interaction between the multiple modes present in the structure.

Besides engineering the absorption spectrum of semiconductor PV devices to match the solar radiation spectrum, I have also explored the idea of modifying solar spectrum to match the PV absorption spectrum[6], [7]. It is presented in chapter three in details. The idea is to convert near-infrared photons into the visible spectrum where semiconductor PV devices can operate efficiently. One good converter, considering the extremely high efficiency compared with all other frequency upconversion mechanisms, is the upconversion nanoparticles (UCNPs) doped with rare-earth ions. They can absorb multiple near-infrared photons, and emit one visible photon. The UCNP I studied is β -NaYF₄:18%Yb³⁺,2%Er³⁺, which is among the most efficient UCNPs. However, the efficiency is still only 4% under 10 W/cm² excitation for micro-size power[70]. It drops further for smaller size particles commonly used in applications such as OPV devices, and bio-imaging. In order to improve the efficiency, people introduce the surface plasmon to enhance the upconverted luminescence. By aligning the surface plasmon resonance at the emission wavelengths, the emission rate can be enhanced up to roughly 10-fold [186], [187].

Placing the surface plasmon resonance at the excitation wavelength, both absorption and energy transfer rate can be enhanced, leading to PL enhancement of several hundreds fold[73], [74]. I designed one-dimensional silver grating structure to support surface plasmon resonance at the excitation wavelength of 980 nm. The steady state PL experiment shows 16-fold enhancement of green emission, and 39-fold enhancement of red emission. The PL enhancement mostly comes from the absorption enhancement, which is only 3-fold. However, the PL enhancement under weak excitation is proportional to the square of absorption enhancement which explains the large PL enhancement we observed. Based on the steady state rate equations analysis, the extra enhancement factor of 1.7-fold comes from the enhanced energy transfer upconversion (ETU) coefficient. To gain deeper understanding of the plasmonic effect on ETU processes, I conducted the transient PL study by both experiment and transient rate equations analysis. I propose an approach to experimentally measure the ETU rate. The results show 2.5-fold enhancement of ETU rate with presence of plasmonics. In addition, I derived the internal upconversion efficiency, which is a quantitative metric of what portion of absorbed excitation photons contributes to the final visible emission. I find that the internal upconversion efficiency increases with stronger excitation power until it reaches saturation. The UCNPs within the plasmonic field can reach ultimate internal upconversion efficiency of 56%, while the UCNPs without plasmonic field can reach ultimate internal upconversion efficiency of 36%. This is the first report of experimentally measured plasmon enhanced ETU rate and internal upconversion efficiency. By the study on steady state PL and transient PL, I demonstrate that plasmonic field can improve the upconverted luminescence by enhancing the absorption, the ETU rate and the internal upconversion efficiency. My work elucidates the mechanism of plasmon enhanced upconverted luminescence, and serves as a guideline for more advanced design in the future.

In the last chapter, I switch the topic from solar energy conversion by traditional semiconductor PV devices to near-field thermal radiation engineering. As we all know, the far-field thermal radiation is limited by the blackbody radiation, where the energy is stored in propagating electromagnetic waves. However, in the near-field, the thermal radiation can far exceed the blackbody radiation[149] thanks to the abundant energy stored in the evanescent waves. Theory has shown that, at the resonance of evanescent waves, the electromagnetic energy density can be six orders of magnitude larger in the near-field than in the far-field regime. It is attractive if people can harvest the gigantic amount of thermal energy residing in the near-field. In order to produce resonant evanescent waves, people have tried excite the surface plasmon polaritons[148], and surface phonon polaritons[147]. However, both of the modes exhibit limited tunability of resonant frequencies. The introduction of spoof surface plasmon polaritons (SSPPs)[159] solves this issue, providing adjustable resonance frequency almost at anywhere[159]. I design a one-dimensional array of grooves in copper that can produce SSPPs at 5 THz under far-field transverse magnetic plane wave excitation. The electric field enhancement in the near-field can reach a maximum of 20-fold compared to the incident field, which corresponds to energy density enhancement of 400-fold. By placing a bow-tie antenna 1 μm away from the metamaterial surface, the electric field at the antenna feed point reaches 30-fold enhancement where the enhancement was only 8-fold without the antenna. The overall energy density is enhanced by close to 1000-fold at the feed point in the final design. Similar work has been done with other designs[168]. However, in the application of near-field thermal energy harvesting, the excitation source is the thermal source instead of the far-field plane wave used in the structure design. The study of thermal excitation of resonant surface waves is scarce in the literature, though it is critical in understanding the near-field thermal radiation properties. The

difficulties lie both in the experiment and modeling. I implemented the thermal modeling based on FDTD method incorporating the Langevin approach to Brownian motion[170]. By applying the thermal excitation modeling to the same structure, the simulation results show the excitation of the same SSPP mode by the near-field thermal source as done by the far-field plane wave excitation. To the best of my knowledge, this is the first demonstration of thermally excited SSPPs. Due to the randomness in polarization of thermal source the coupling to SSPPs is about 50% weaker than the far-field plane wave excitation. But still I observed 400-fold enhancement of energy density compared to that of blackbody body radiation. I believe that much higher near-field energy density is achievable with more advanced designs. The significance of potential applications and interesting physics behind it make the near-field energy radiation a very promising topic.

6 Appendix

6.1 Atomic force microscopy data for LBL UCNP layer thicknesses

The UCNP particles possess hexagonal platelet shape and TEM only shows the lateral size. Therefore it is necessary to measure the actual thicknesses of LBL deposited layers. We conducted a series of atomic force microscopy scans to determine the thickness of one, three and five monolayers of UCNP samples. As shown in Fig. 6.1, the thickness increased linearly with the number of layers. The three-layer sample, which was used in this paper, had a thickness of 90 ± 2 nm.

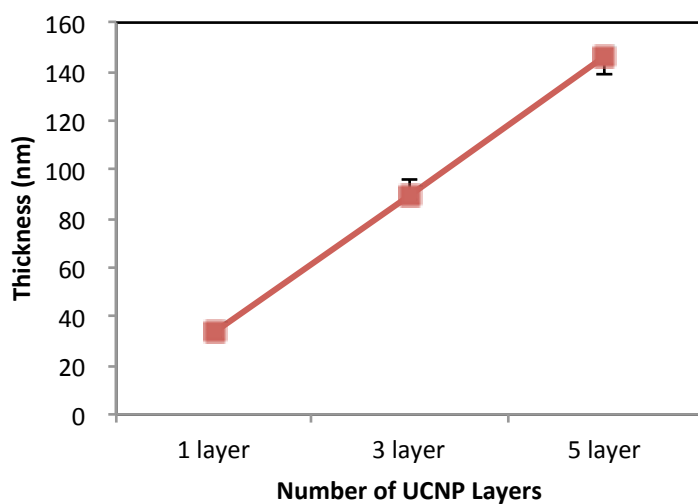


Figure 6.1 Atomic force microscopy measurements of thicknesses of 1, 3 and 5 layer UCNP films deposited by the LBL method.

6.2 PL spectroscopy experiment

6.2.1 Steady-state PL spectroscopy

I excite the UCNPs samples with a 980 nm laser diode (OEM laser) normally incident on the sample surface. The polarization is in the direction orthogonal to silver nanograting lines to excite the surface plasmon modes. For visible PL measurement, the excitation light reflected off the sample surface is rejected by a dichroic mirror (Thorlabs DMSP 805) while the visible PL signal is transmitted through the dichroic mirror and collimated by a convex lens with focal length of 5 cm. The collimated PL signal is then focused by another convex lens into the entrance slit of spectrometer (Acton SpectraPro 300i). A liquid nitrogen cooled Si CCD (Roper Scientific) is equipped with the spectrometer to detect and record the PL spectrum. In order to protect the detector from any stray laser light, short-pass edge filters (Scott KG5) are placed right before the spectrometer entrance slit. Same setup is used for NIR PL measurement with minor changes. The excitation laser is first cleaned up by a band-pass filter (Semrock LL01-980) with 3.7 nm bandwidth centered at 980 nm. Then, I use NIR beam splitter cube, instead of dichroic mirror, to reflect the excitation laser to samples. The emitted PL signal from the sample passes through the beam splitter cube, and get collected to the spectrometer. In order to protect the NIR detector (Andor iDus InGaAs), I put one long-pass filter (Semrock BLP01-980R) before the monochromator entrance slit to attenuate the laser light and pass only the NIR emission from UCNPs.

6.2.2 Time-resolved PL spectroscopy

In the time-resolved PL spectroscopy, a square pulse train of 980 nm light from laser diode (Thorlabs L980P200) is used to excite UCNPs samples at normal incidence. The laser pulse duration and duty cycle are controlled by a function generator (Wavetek model 166) connected

to the laser diode current driver (Thorlabs TCLDM9). For the transient NIR PL reported in this paper, I used a square wave with 20 ms period and 50% duty cycle. A band-pass filter (Semrock LL01-980) with 3.7 nm bandwidth centered at 980 nm is placed in front of the laser to filter out side band emissions. Then, the cleaned laser beam is expanded by a 5x achromatic Galilean beam expander to the diameter around 1 cm before it is focused tightly onto the sample surface. The excitation laser beam is directed onto the sample at normal incidence using a NIR beam splitter cube. For the plasmonic nanograting sample, I align the laser polarization orthogonal to the nanograting lines. The emission from the UCNPs is collimated and re-focused to a monochromator (Sciencetech 9057F) by two convex lenses. For transient NIR PL detection, I place one long-pass filter (Semrock BLP01-980R) before the monochromator entrance slit to attenuate the laser light and pass only the NIR emission from UCNPs. The monochromator is set at 1002 nm and the transient PL signal is recorded by a NIR photomultiplier tube (Hamamatsu H10330B-75), which is connected to a photon counter (Stanford Research Systems SR430). The photon counter input is synchronized with the laser pulse by the function generator, and the transient NIR PL is stored in the internal memory of photon counter. The same setup is also used for the transient green PL detection with the same 980 nm laser pulse excitation except that I replace the long-pass filter (Semrock BLP01-980R) by short-pass edge filters (Scott KG5), and deliver 550 nm light to visible PMT (Hamamatsu H11461P-11). The 980 nm laser excitation power is adjusted by the function generator output to laser diode current drive. I also measured the transient green PL under green laser (Thorlabs, DJ532-40) excitation at 532 nm using the same setup. The side band of excitation green laser is filtered by band-pass filter (Semrock FF01-524/24). Before the monochromator entrance, the excitation green laser is attenuated by long-

pass filter (BLP01-532R-25). For the green laser pulses, the square waveform has a period of 40 ms with 50% duty cycle.

6.3 Solutions to the steady-state rate equations

For completeness, I rewrite the full set of rate equations given in Chapter three.

$$\frac{dN_{D1}}{dt} = \sigma \Phi N_{D0} - W_{D10} N_{D1} + c_{Bd2} N_{A2} N_{D0} - c_{Fd2} N_{D1} N_{A0} - c_{d3} N_{D1} N_{A1} - c_{d4} N_{D1} N_{A2} \quad (6.1)$$

$$\frac{dN_{A1}}{dt} = W_{A21} N_{A2} - W_{A10} N_{A1} - c_{d3} N_{D1} N_{A1} \quad (6.2)$$

$$\frac{dN_{A2}}{dt} = c_{Fd2} N_{D1} N_{A0} - c_{Bd2} N_{A2} N_{D0} - c_{d4} N_{D1} N_{A2} - W_{A20} N_{A2} - W_{A21} N_{A2} \quad (6.3)$$

$$\frac{dN_{A3}}{dt} = W_{A43} N_{A4} + c_{d3} N_{A1} N_{D1} - W_{A30} N_{A3} \quad (6.4)$$

$$\frac{dN_{A4}}{dt} = c_{d4} N_{D1} N_{A2} - W_{A40} N_{A4} - W_{A43} N_{A4} \quad (6.5)$$

$$N_D = N_{D0} + N_{D1} \quad (6.6)$$

$$N_A = N_{A0} + N_{A1} + N_{A2} + N_{A3} + N_{A4} \quad (6.7)$$

Here N_i is the density of ions in the energy level i . The subscripts D1 and D0 represent the $^2F_{5/2}$ and $^2F_{7/2}$ levels of donor (Yb^{3+}), respectively, and A4, A3, A2, A1, and A0 indicate the $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$ levels of acceptor (Er^{3+}), respectively. W is the decay rate and the subscript indicates the initial and final states of the transition. For example, W_{D10} is the decay rate of donor ion from D1 to D0 state. c_{d2} , c_{d3} and c_{d4} are the energy transfer coefficients for the Förster energy transfer processes between the donor and the acceptor in A2, A3 and A4 levels, respectively. The additional subscripts, F and B, in the c_{d2} coefficient indicate the forward (donor to acceptor) and

backward (acceptor to donor) energy transfers. Finally, N_D and N_A are the doping densities of donor and acceptor, respectively, σ is the absorption cross section of the donor ion, and Φ is the incident light flux.

In the steady state achievable under continuous-wave (cw) excitation, all time derivatives are zero. In the weak excitation limit, the densities of excited ions would be small and the decay processes are more efficient than upconversion. Thus, we may ignore $c_{d3}N_{D1}N_{A1}$ and $c_{d4}N_{D1}N_{A2}$ terms in equations (3.1) ~ (6.3). Also the ground state populations of the donor and acceptor should be equal to the doping densities.

$$\frac{dN_{D1}}{dt} = 0 = \sigma\Phi N_{D0} - W_{D10}N_{D1} + c_{Bd2}N_{A2}N_{D0} - c_{Fd2}N_{D1}N_{A0} \quad (6.8)$$

$$\frac{dN_{A1}}{dt} = 0 = W_{A21}N_{A2} - W_{A10}N_{A1} \quad (6.9)$$

$$N_D = N_{D0} \quad (6.10)$$

$$N_A = N_{A0} \quad (6.11)$$

Equations (6.4)~(6.5) remain the same. From equations (6.8) and (6.3), we obtain,

$$0 = \sigma\Phi N_D - W_{D10}N_{D1} - W_{A20}N_{A2} - W_{A21}N_{A2} = \sigma\Phi N_D - W_{D10}N_{D1} - W_{A2}N_{A2} \quad (6.12)$$

where $W_{A2} = W_{A20} + W_{A21}$. From equations (6.3), (6.9) and (6.12), we find,

$$N_{D1} = \frac{c_{Bd2}N_D + W_{A2}}{c_{Fd2}N_A} N_{A2} \quad (6.13)$$

$$N_{A2} = \frac{\sigma\Phi N_D}{W_{A2} + W_{D10} \left(\frac{c_{Bd2}N_D + W_{A2}}{c_{Fd2}N_A} \right)} \quad (6.14)$$

$$N_{A1} = \frac{W_{A21}}{W_{A10}} N_{A2} \quad (6.15)$$

Now we are ready to write the expressions for the green and red emission intensities. The green photon emission rate is given by,

$$\Phi_G = W_{A40} N_{A4} = \frac{W_{A40}}{W_{A4}} c_{d4} N_{D1} N_{A2} \quad (6.16)$$

where $W_{A4} = W_{A40} + W_{A43}$. Substituting equations (6.13) and (6.14) into (6.16) gives

$$\Phi_G = \frac{W_{A40}}{W_{A4}} \frac{c_{d4} (c_{Bd2} N_D + W_{A2}) N_D^2}{c_{Fd2} N_A [W_{A2} + W_{D10} (c_{Bd2} N_D + W_{A2}) / c_{Fd2} N_A]} (\sigma\Phi)^2 \quad (6.17)$$

Similarly, the red photon emission rate is found to be,

$$\begin{aligned} \Phi_R &= W_{A30} N_{A3} = W_{A43} N_{A4} + c_{d3} N_{D1} N_{A1} = \frac{W_{A43}}{W_{A4}} c_{d4} N_{D1} N_{A2} + \frac{W_{A21}}{W_{A10}} c_{d3} N_{D1} N_{A2} \\ &= \left(\frac{W_{A43} c_{d4}}{W_{A4}} + \frac{W_{A21} c_{d3}}{W_{A10}} \right) \frac{(c_{Bd2} N_D + W_{A2}) N_D^2}{c_{Fd2} N_A (W_{A2} + W_{D10} (c_{Bd2} N_D + W_{A2}) / c_{Fd2} N_A)^2} \cdot (\sigma\Phi)^2 \end{aligned} \quad (6.18)$$

Although the equations (6.17) and (6.18) are rather complex, they clearly show the quadratic dependence on the incident photon flux consistent with the experimental data. For further simplifications, we compare the back transfer rate, $c_{Bd2} N_D$, and the decay rate for A2 level, W_{A2} . Due to the forbidden nature of f-f transition, W_{A2} is slow and known to be of the order of 10^3 s^{-1} . [70] In our case, the presence of metal surface introduces strong nano-radiative decay path, increasing W_{A2} . From the experimentally measured PL decay in the NIR presented in Fig. 3.5(b) and Fig. 3.7, we anticipate W_{A2} is on the order of 10^4 s^{-1} in our samples. The back transfer coefficient, c_{Bd2} , has been reported to be $\sim 10^{-16} \text{ cm}^3/\text{s}$ for Yb-Er co-doped systems. [85], [91] Since our donor density is $2 \times 10^{21} \text{ cm}^{-3}$, we have $c_{Bd2} N_D$ between $\sim 10^5 \text{ s}^{-1}$, at least one order of magnitude greater than W_{A2} . Furthermore, since we have $W_{D10} \approx W_{A2}$, $c_{Fd2} \approx c_{Bd2}$ and $N_D \gg N_A$, we finally obtain reasonably simple expressions for the green and red emission.

$$\Phi_G = \frac{W_{A40}}{W_{A4}} \frac{c_{d4} c_{Fd2} N_A N_D}{c_{Bd2} W_{D10}^2} \cdot (\sigma\Phi)^2 \quad (6.19)$$

$$\Phi_R = \left(\frac{W_{A43} c_{d4}}{W_{A4}} + \frac{W_{A21} c_{d3}}{W_{A10}} \right) \frac{c_{Fd2} N_A N_D}{c_{Bd2} W_{D10}^2} \cdot (\sigma\Phi)^2 \quad (6.20)$$

In addition to the quadratic dependence on the excitation power density, equations (6.19) and (6.20) show the upconverted luminescence intensity should increase linearly with the donor and acceptor densities. Also, the upconverted luminescence intensity varies linearly with the energy transfer coefficients, c_{Fd2} , c_{d3} and c_{d4} , and inversely with c_{Bd2} and the square of donor decay rate, W_{D10} . These simplified expressions provide the basis for determining the plasmon enhancement effects on various processes as discussed later.

For the strong excitation limit, I first rearrange equations (3.1) and (6.3) as follows.

$$\begin{aligned} 0 &= \sigma\Phi N_{D0} - W_{D10} N_{D1} - c_{d3} N_{D1} N_{A1} - 2c_{d4} N_{D1} N_{A2} - W_{A20} N_{A2} - W_{A21} N_{A2} \\ &= \sigma\Phi N_{D0} - W_{D10} N_{D1} - 2W_{A21} N_{A2} - W_{A20} N_{A2} + W_{A10} N_{A1} - 2c_{d4} N_{D1} N_{A2} \end{aligned} \quad (6.21)$$

In the strong excitation limit, the energy transfer processes dominate over the decay processes and we thus ignore all decay terms and only retain energy transfer terms in equations (6.21). [86]

$$0 = \sigma\Phi N_{D0} - 2c_{d4} N_{D1} N_{A2} \quad (6.22)$$

Finally, the green photon emission rate is given as,

$$\Phi_G = W_{A40} N_{A4} = \frac{W_{A40}}{W_{A4}} c_{d4} N_{D1} N_{A2} = \frac{W_{A40}}{W_{A4}} \frac{N_{D0}}{2} \sigma\Phi \quad (6.23)$$

For the red photon emission rate, it contains two terms as shown in equation (6.18): one branching off A4 level and the other branching off A2 level. In the strong excitation limit, the energy transfer upconversion should generally dominate over decays and thus the decay of

acceptor ion from A2 level to A1 level should be small compared to the upconversion into the A4 level, i.e. N_{A1} is very small. Thus the red photon emission rate can be written as,

$$\Phi_R = \frac{W_{A43}}{W_{A4}} c_{d4} N_{A2} N_{D1} + c_{d3} N_{A1} N_{D1} \simeq \frac{W_{A43}}{W_{A4}} c_{d4} N_{A2} N_{D1} = \frac{W_{A43}}{W_{A4}} \frac{N_{D0}}{2} \sigma \Phi \quad (6.24)$$

Equations (3.10) and (3.11) show the linear power dependence on the excitation power density as observed in experiments. Also, it is important to note that the upconverted luminescence intensity depends only on the donor density and excitation power density but not on any of the energy transfer coefficients.

6.4 Calculation of energy transfer rate enhancement near a silver surface

As given in the Chapter three, the Förster energy transfer rate for a donor-acceptor pair in a dispersive and absorbing medium given by

$$W_{ET} = \int d\omega \sigma_A(\omega) \sigma_D(\omega) \tilde{w}(\omega) \quad (6.25)$$

where σ_A and σ_D are the free-space absorption and emission spectra of acceptor and donor, respectively. The information about the medium is contained in $\tilde{w}(\omega)$, which can be expressed in terms of the dyadic Green function as follows

$$\tilde{w}(\omega) = \frac{2\pi}{\hbar^2} \frac{\omega^2}{\epsilon_0 c^2} \left| \mathbf{d}_A^* \cdot \mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) \cdot \mathbf{d}_D \right|^2 \quad (6.26)$$

If the dyadic Green function varies slowly with frequency compared to the linewidth of the absorption and emission spectra of acceptor and donor, the energy transfer rate can be approximately expressed in terms of the Green function evaluated at the energy transfer frequency, $\omega_D \approx \omega_A$, as

$$W_{ET} = \tilde{w}(\omega_D) \int d\omega \sigma_A(\omega) \sigma_D(\omega) \quad (6.27)$$

The dyadic Green function for a donor-acceptor pair placed close to a planar interface between two media can be expressed as

$$\mathbf{G}(\mathbf{r}_A, \mathbf{r}_D, \omega) = \mathbf{G}^{bulk}(\mathbf{r}_A, \mathbf{r}_D, \omega) + \mathbf{G}^{refl}(\mathbf{r}_A, \mathbf{r}_D, \omega) \quad (6.28)$$

where $\mathbf{G}^{bulk}(\mathbf{r}_A, \mathbf{r}_D, \omega)$ is the Green function for uniform space and $\mathbf{G}^{refl}(\mathbf{r}_A, \mathbf{r}_D, \omega)$ is the Green function representing the contribution from the interface. Dung et al. {Dung:2002dr} derived analytical expressions for $\mathbf{G}^{refl}(\mathbf{r}_A, \mathbf{r}_D, \omega)$ when both the donor-acceptor pair separation and their distance from the interface are small compare to the wavelength.

$$\begin{aligned} G_{xx,yy}^{refl} &= \frac{1}{4\pi k_1^2} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \frac{(z_D + z_A)^2 \pm 2(x_D - x_A)^2}{\left[(z_D + z_A)^2 + 2(x_D - x_A)^2\right]^{5/2}} \\ G_{xz,zx}^{refl} &= \pm \frac{1}{4\pi k_1^2} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \frac{3(z_D + z_A)(x_D - x_A)}{\left[(z_D + z_A)^2 + (x_D - x_A)^2\right]^{5/2}} \\ G_{zz}^{refl} &= \pm \frac{1}{4\pi} \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \frac{1}{\sqrt{(z_D + z_A)^2 + (x_D - x_A)^2}} \left\{ \frac{2(z_D + z_A)^2 - (x_D - x_A)^2}{k_1^2 \left[(z_D + z_A)^2 + (x_D - x_A)^2\right]^2} + 1 \right\} \end{aligned} \quad (6.29)$$

where ϵ_1 and ϵ_2 are the permittivities of the two media (donor-acceptor pair is embedded in ϵ_1), k_1 is the wave number in medium 1, and x and z are the coordinates of the donor and the acceptor as indicated by the subscript. Using theses expressions, we now calculate energy transfer rate enhancement for a donor-acceptor pair embedded in a dielectric medium of refractive index 1.3 and placed close to a silver surface. Fig. 6.2 shows the energy transfer rate enhancement factor for a donor-acceptor pair separated by 3.4 nm, which is our lower bound estimate for r_{A2} . In this system, the surface plasmon frequency at which $\epsilon_1 = -\text{Re}(\epsilon_2)$ corresponds to 340 nm. As shown, there can be a significant enhancement at frequencies slightly lower than the surface plasmon frequency. The enhancement is larger for shorter distances from the metal surface. Additionally, the enhancement factor was calculated for various donor-acceptor distances, as shown in Fig.

6.3, while the donor-metal distance was fixed at $0.03\lambda_{sp}$. The enhancement varies greatly for different donor-acceptor orientations but in general the enhancement begins to emerge at a distance of 2 nm and increases with increasing donor-acceptor distance. These results do not represent the anticipated enhancement in the energy transfer rate in our nanograting sample. However, they do show that the energy transfer rate is enhanced near plasmon resonance frequency and suggest it is likely that the energy transfer rate is enhanced in the nanograting sample.

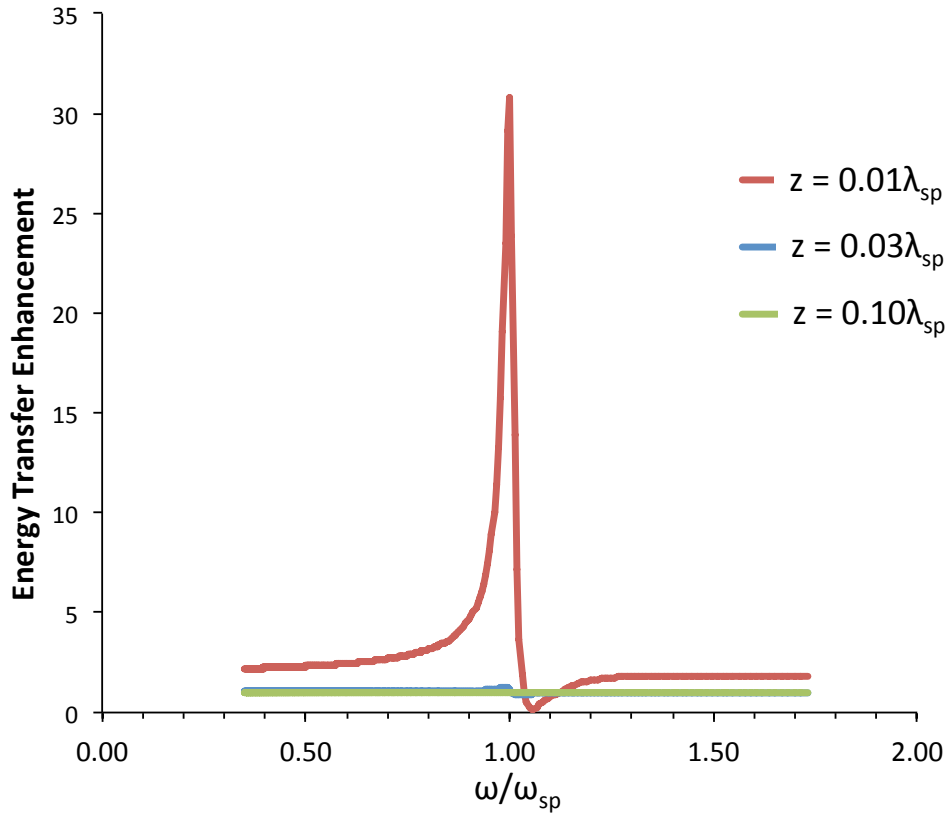


Figure 6.2 Energy transfer rate enhancement factor calculated for a donor-acceptor pair with a pair separation of 3.4 nm placed at various distances, z , from the silver surface. ω_{sp} and λ_{sp} represent the surface plasmon frequency and wavelength, respectively. For the present case, $\lambda_{sp} = 340$ nm.

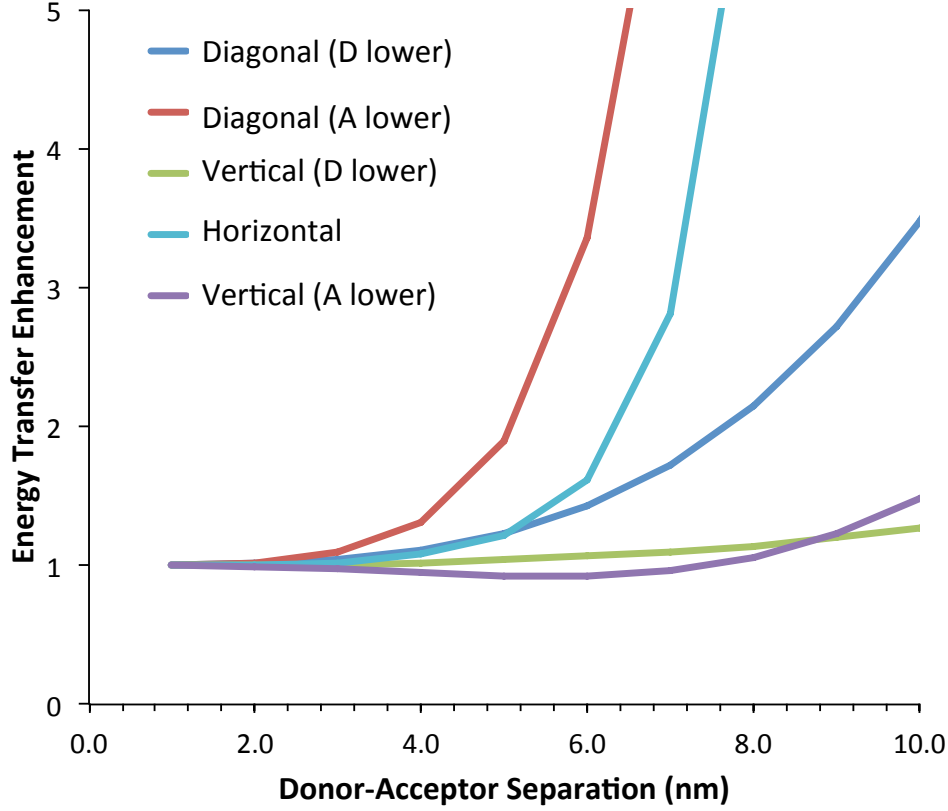


Figure 6.3 Energy transfer rate enhancement factor as a function of donor-acceptor distance. The donor is placed at $0.03l_{sp}$ away from the metal surface where $l_{sp} = 340$ nm. In the legend, horizontal corresponds to xx, yy case in Eq. (6.29). Diagonal data corresponds to xz, zx case in Eq. (6.29). Vertical corresponds to zz case in Eq. (6.29).

6.5 Purcell factor calculation based on finite element modeling

I evaluated Purcell factor following the method by Gong *et al.*[128] from the finite element modeling results. The Purcell factor was calculates as,

$$F = \frac{3}{4\pi^2} \left(\frac{\lambda}{n} \right)^3 \frac{Q}{V_{spp}} \overline{\left(\frac{E}{E_{\max}} \right)^2} \quad (6.30)$$

where n is the refractive index of UCNP layer, Q is the quality factor extracted from the measured reflectance spectra in Fig. 3.2a. The E-field was averaged over the UCNP layer, and V_{spp} is the surface plasmon mode volume which was calculated by

$$V_{spp} = \frac{\iint \epsilon_E |E(x, z)|^2 dx dz}{\max \left[\epsilon_E |E(x, z)|^2 \right]} Y \quad (6.31)$$

The integral is over one period of the surface plasmon mode as shown in Fig. 3.2(a) inset.

ϵ_E is the effective dielectric constant with expression of $\epsilon_E = d(\omega \epsilon) / d\omega$. Y is the length of grating which was illuminated in reflectance spectrum measurement. In our case, it was around 200 μm .

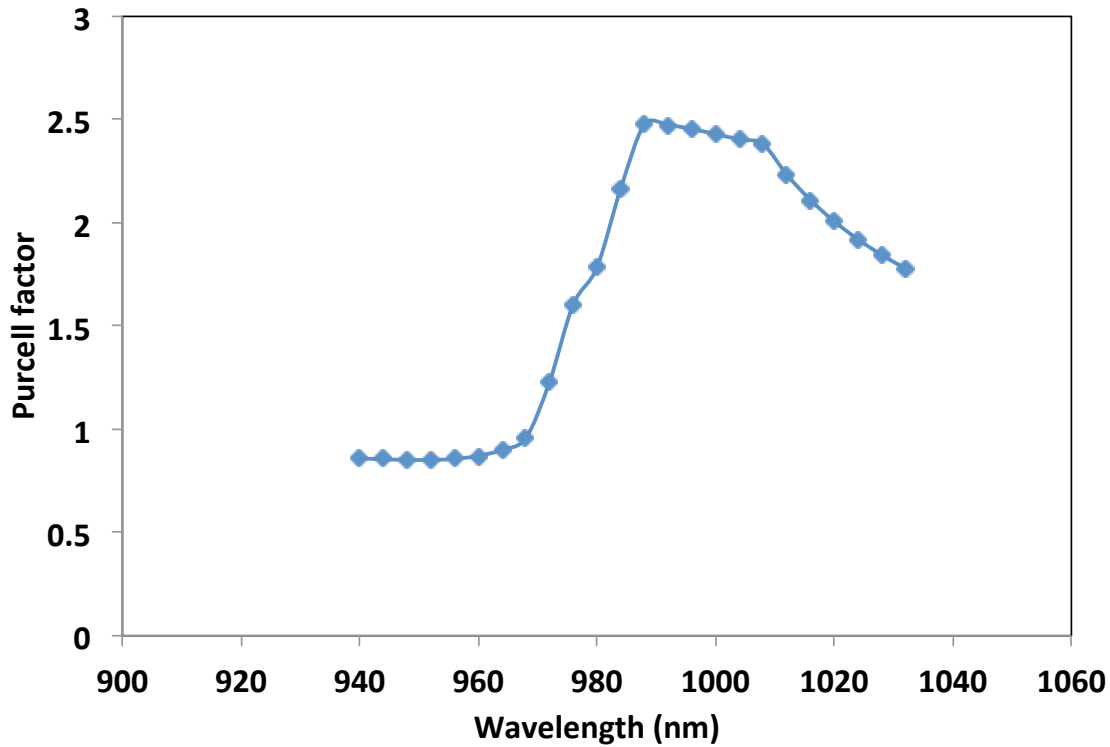


Figure 6.4 Purcell factor of UCNP on nanograting due to the excitation of surface plasmon mode. The Purcell factor reaches maximum of 2.48 at 988 nm. The Purcell factor at 980 nm was 1.78.

6.6 Emission pattern calculation based on finite element modeling

The emission patterns of the naongrating and reference samples were also obtained from finite element modeling (COMSOL Multiphysics). Basically, I put a dipole source with emission wavelength of 550 nm (UCNP green emission band) at the center of UCNP layer and calculated the emitted power within the solid angle captured by our collection lens (NA = 0.13) used in PL measurements. To take into account the random polarization of UCNP emission, I repeated this calculation over different dipole polarization orientations with 15-degree intervals and obtained an average. The difference was negligibly small, ~4%.

6.7 Rate equation analysis of the NIR PL decay.

The NIR PL decay follows the same equation as the rise except the pumping term:

$$\frac{dN_{D1}}{dt} = -W_{D10}N_{D1} - c_{d3}N_{D1}N_{A1} - 2c_{d4}N_{D1}N_{A2} \quad (6.32)$$

During the decay process, the population of N_{A2} and N_{A1} can be approximated by single exponential as $N_{A2}(t) = N_{A2}^0 e^{-W_{A2}t}$ and $N_{A1}(t) = N_{A1}^0 e^{-W_{A1}t}$, respectively. Here, N_{A2}^0 and N_{A1}^0 are the steady state population of intermediate energy levels A_2 and A_1 at $t = 0$, and W_{A2} and W_{A1} are the corresponding decay rates. Directly solving the equation (6.32), I obtained the normalized population of N_{D1}

$$N_{D1}(t) = \exp \left[-W_{D10}t - \frac{2c_{d4}N_{A2}^0}{W_{A2}}(1 - e^{-W_{A2}t}) - \frac{c_{d3}N_{A1}^0}{W_{A1}}(1 - e^{-W_{A1}t}) \right] \quad (6.33)$$

For $t \ll \min\{1/W_{A2}, 1/W_{A1}\}$, the normalized population of N_{D1} can be approximated by

$$N_{D1}(t) = \exp\left[-(W_{D10} + 2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0)t\right] \quad (6.34)$$

The total decay rate $W_{D1,decay}$ of NIR PL is then given as,

$$W_{D1,decay} = W_{D10} + 2c_{d4}N_{A2}^0 + c_{d3}N_{A1}^0 \quad (6.35)$$

This is exactly the same as the rise rate expressed in equation (3.26), except for the excitation term.

6.8 Rate equation analysis of the green PL decay

The decay curves of green emission under 980 nm laser excitation are shown in Fig. 6.5 for the nanograting and reference samples. Again, I observed slow decay at the beginning as a result of competition between upconversion and decay. Later, all decay curves follow the intrinsic decay as shown in green line in Fig. 6.5.

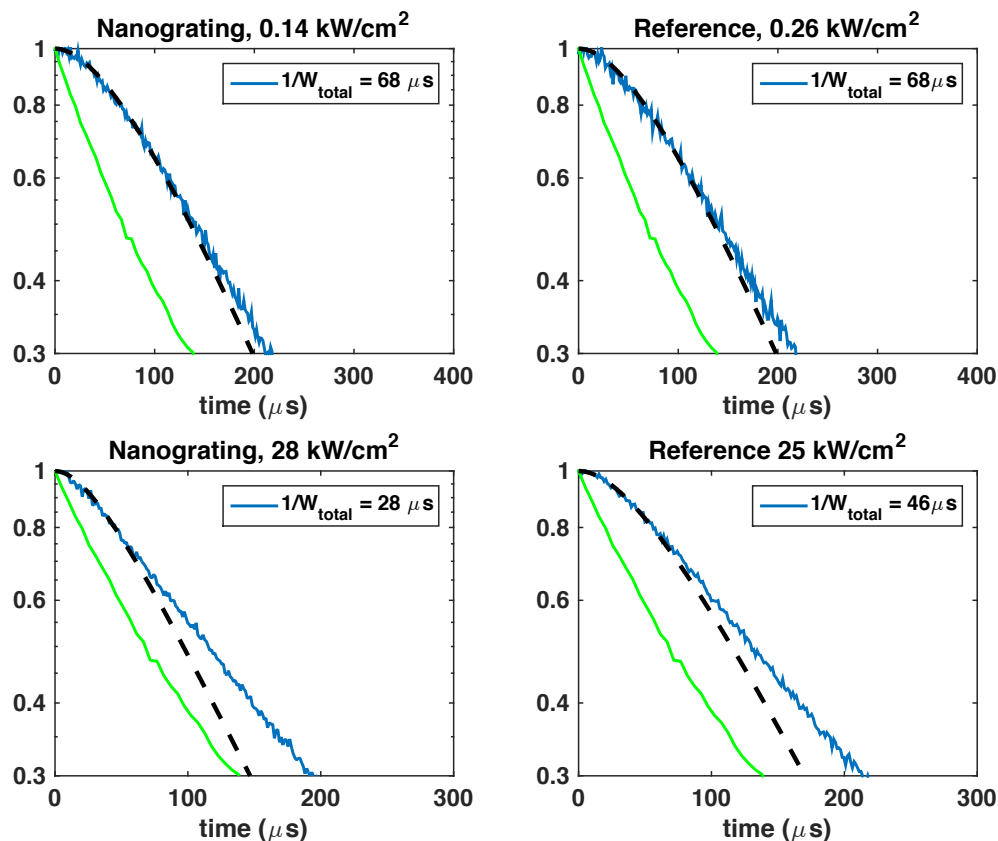


Figure 6.5 Green emission decay (blue lines) of UCNP on nanograting (nanograting sample) and on silver film (reference sample) under weak and strong excitation power densities. The green emission decay of UCNP upon green laser excitation is a single exponential decay with a decay time of 95 μs (green line). The black dash lines are the fittings using Eq.(6.38). All experimental PL decay curves are normalized with the steady state PL intensities, and plotted in logarithmic scale.

The equation (3.28) in Chapter three applies for green emission decay process as well. I re-write it here:

$$\frac{dN_{A4}}{dt} = c_{d4}N_{D1}N_{A2} - W_{A4}N_{A4} \quad (6.36)$$

The description and the values of the coefficients can be found in manuscript. In the decay process, the intermediate energy level population, N_{D1} and N_{A2} , can be approximated by single exponential decay: $N_{D1}(t) = N_{D1}^0 e^{-W_{D1}t}$ and $N_{A2}(t) = N_{A2}^0 e^{-W_{A2}t}$, where N_{D1}^0 and N_{A2}^0 are

the steady state population of $D1$ and $A2$ levels at $t = 0$, and W_{D1} and W_{A2} are the decay rate of N_{D1} and N_{A2} respectively. The ETU term can then be written as,

$$c_{d4}N_{D1}N_{A2} = c_{d4}N_{D1}^0N_{A2}^0e^{-(W_{D1}+W_{A2})t} \quad (6.37)$$

Substituting this expression for $c_{d4}N_{D1}N_{A2}$ into Eq. (6.36), and solving for the normalized decay expression of green emission yields,

$$N_{A4}(t) = \frac{W_{A4}}{W_{A4} - W_{total}} \left[e^{-W_{total}t} - \frac{W_{total}}{W_{A4}} e^{-W_{A4}t} \right] \quad (6.38)$$

where W_{total} is the sum of decay rates W_{D1} and W_{A2} .

The experimentally measured green decay was fitted by Eq. (6.38) to extract the total decay rate W_{total} . Since I had measured the NIR emission decay of donor ions W_{D1} , I can subtract it from W_{total} to obtain acceptor ion NIR decay rate W_{A2} . The results are listed in Table 6-1. As we can see, the NIR decay rates of acceptor ions equal to its rise rates presented in the manuscript. And once again the ratio of NIR decay rates of acceptor ions to that of donor ions stay constant at 1.5 irrespective of the excitation conditions.

	Nanograting, 0.14 kW/cm ²	Reference, 0.26 kW/cm ²	Nanograting, 28 kW/cm ²	Reference, 25 kW/cm ²
W_{total}	$1.47 \times 10^4 \text{ s}^{-1}$	$1.47 \times 10^4 \text{ s}^{-1}$	$3.57 \times 10^4 \text{ s}^{-1}$	$2.17 \times 10^4 \text{ s}^{-1}$
W_{D1}	$5.88 \times 10^3 \text{ s}^{-1}$	$5.88 \times 10^3 \text{ s}^{-1}$	$1.41 \times 10^4 \text{ s}^{-1}$	$8.93 \times 10^3 \text{ s}^{-1}$
$W_{A2}=W_{total}-W_{D1}$	$8.85 \times 10^3 \text{ s}^{-1}$	$8.85 \times 10^3 \text{ s}^{-1}$	$2.16 \times 10^4 \text{ s}^{-1}$	$1.28 \times 10^4 \text{ s}^{-1}$
W_{A2}/W_{D1}	1.51	1.51	1.53	1.43

Table 6-1 The sample information and excitation conditions are listed in first row. The total NIR decay rates obtained from the green emission decay at different excitation power densities are listed on the second row. The third row shows the NIR decay rate of donor ions from NIR PL analysis presented in

manuscript. The acceptor ions NIR decay rates W_{A2} are listed on fourth row. The last row shows the ratio of acceptor NIR decay rates to donor NIR decay rates.

6.9 Temperature of UCNP's under excitation

As described in Chapter three, the UCNP temperature can be extracted from the ratio of two green emission bands (I_S : $^4S_{3/2} \rightarrow ^4I_{15/2}$, I_H : $^4H_{11/2} \rightarrow ^4I_{15/2}$)

$$I_H / I_S = C \exp(-\Delta E / k_B T)$$

Here, $\Delta E = 600 \text{ cm}^{-1}$ is the energy gap between level $^4S_{3/2}$ and $^4H_{11/2}$, and C is constant.

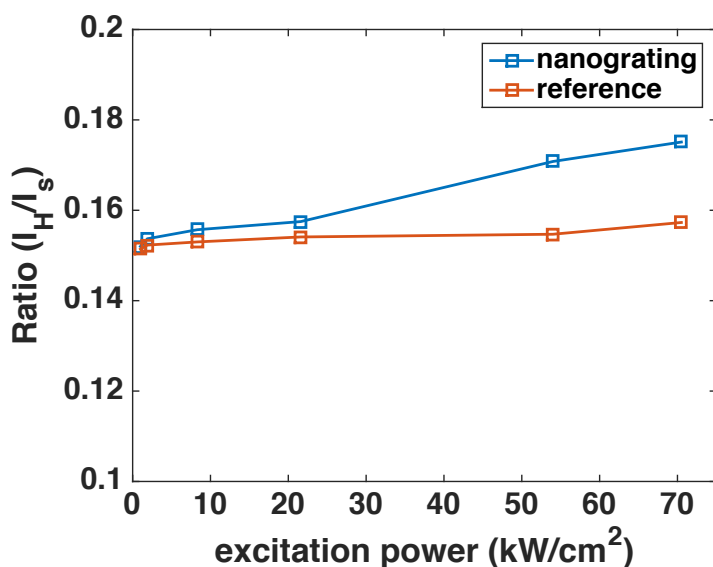


Figure 6.6 Intensity ratio of two green emission band under different excitation power densities for nanograting sample and reference samples.

The ratio, I_H/I_S , is shown in Fig. 6.6 for all excitation conditions used in this paper, $1 \text{ kW/cm}^2 \sim 61 \text{ kW/cm}^2$. Assuming the temperature of the sample under the weakest excitation (1 kW/cm^2) is equal to the room temperature, 300K, I obtain the sample temperatures under all other excitation conditions as shown in Fig. 6.7.

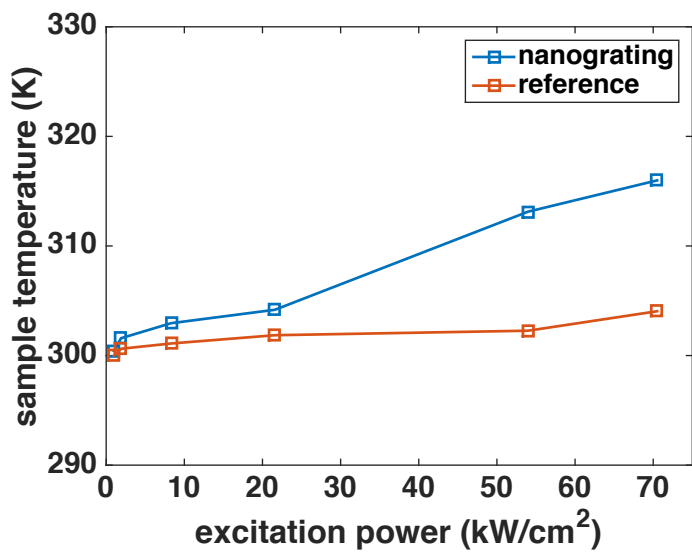


Figure 6.7 Sample temperature under various excitation conditions

7 References

- [1] E. J. Zeman and G. C. Schatz, “An accurate electromagnetic theory study of surface enhancement factors for Ag, Au, Cu, Li, Na, Al, Ga, In, Zn, and Cd,” *J. Phys. Chem.*, vol. 91, no. 3, pp. 634–643, 1987.
- [2] W. L. Barnes, A. Dereux, and T. W. Ebbesen, “Surface plasmon subwavelength optics,” *Nature*, vol. 424, no. 6950, pp. 824–830, 2003.
- [3] R. B. Dunbar, T. Pfadler, and L. Schmidt-Mende, “Highly absorbing solar cells—a survey of plasmonic nanostructures,” *Opt. Express*, vol. 20, p. 177, Mar. 2012.
- [4] H. A. Atwater and A. Polman, “Plasmonics for improved photovoltaic devices,” *Nat. Mater.*, vol. 9, no. 3, pp. 205–213, Feb. 2010.
- [5] D. Lu, E. Rengnath, Y. Cui, Z. Wang, Y. Ding, and W. Park, “Interaction of two plasmon modes in the organic photovoltaic devices with patterned back-electrode,” *Appl. Phys. Lett.*, vol. 102, no. 24, pp. 241114–241114, Jun. 2013.
- [6] D. Lu, S. K. Cho, S. Ahn, L. Brun, C. J. Summers, and W. Park, “Plasmon enhancement mechanism for the upconversion processes in $\text{NaYF}_4:\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles: Maxwell versus Förster,” *ACS Nano*, vol. 8, no. 8, pp. 7780–7792, Aug. 2014.
- [7] W. Park, D. Lu, and S. Ahn, “Plasmon enhancement of luminescence upconversion,” *Chem. Soc. Rev.*, vol. 44, no. 10, pp. 2940–2962, 2015.
- [8] M. Saboktakin, X. Ye, U. K. Chettiar, N. Engheta, C. B. Murray, and C. R. Kagan, “Plasmonic enhancement of nanophosphor upconversion luminescence in Au nanohole arrays,” *ACS Nano*, vol. 7, no. 8, pp. 7186–7192, Aug. 2013.
- [9] W. A. Challener, C. Peng, A. V. Itagi, D. Karns, W. Peng, Y. Peng, X. Yang, X. Zhu, N. J. Gokemeijer, Y. T. Hsia, G. Ju, R. E. Rottmayer, M. A. Seigler, and E. C. Gage, “Heat-assisted magnetic recording by a near-field transducer with efficient optical energy transfer,” *Nat. Photonics*, vol. 3, no. 4, pp. 220–224, Apr. 2009.
- [10] N. Fang, H. Lee, C. Sun, and X. Zhang, “Sub-diffraction-limited optical imaging with a silver superlens,” *Science*, vol. 308, no. 5721, pp. 534–537, 2005.
- [11] Z. Liu, S. Durant, H. Lee, Y. Pikus, N. Fang, Y. Xiong, C. Sun, and X. Zhang, “Far-field optical superlens,” *Nano Lett.*, vol. 7, no. 2, pp. 403–408, Feb. 2007.
- [12] X. Zhang and Z. Liu, “Superlenses to overcome the diffraction limit,” *Nat. Mater.*, vol. 7, no. 6, pp. 435–441, Jun. 2008.
- [13] M. L. Juan, M. Righini, and R. Quidant, “Plasmon nano-optical tweezers,” *Nat. Photonics*, vol. 5, no. 6, pp. 349–356, Jun. 2011.
- [14] K. Joulain, R. Carminati, J. P. Mulet, and J. J. Greffet, “Definition and measurement of the local density of electromagnetic states close to an interface,” *Phys. Rev. B*, vol. 68, no. 24, Dec. 2003.
- [15] A. Shchegrov, K. Joulain, R. Carminati, and J. Greffet, “Near-field spectral effects due to electromagnetic surface excitations,” *Phys. Rev. Lett.*, vol. 85, no. 7, pp. 1548–1551, Aug. 2000.
- [16] A. Narayanaswamy and G. Chen, “Surface modes for near field thermophotovoltaics,” *Appl. Phys. Lett.*, vol. 82, no. 20, p. 3544, May 2003.
- [17] M. Laroche, R. Carminati, and J. J. Greffet, “Near-field thermophotovoltaic energy conversion,” *J. Appl. Phys.*, vol. 100, no. 6, p. 3704, Sep. 2006.

- [18] E. M. Purcell, "Spontaneous emission probabilities at radio frequencies," *Physical Review*, vol. 69, p. 681, 1946.
- [19] M. Kuttge, E. J. R. Vesseur, A. F. Koenderink, H. J. Lezec, H. A. Atwater, F. J. García de Abajo, and A. Polman, "Local density of states, spectrum, and far-field interference of surface plasmon polaritons probed by cathodoluminescence," *Phys. Rev. B*, vol. 79, no. 1, p. 113405, Mar. 2009.
- [20] D. E. Chang, A. S. Sørensen, P. R. Hemmer, and M. D. Lukin, "Strong coupling of single emitters to surface plasmons," *Phys. Rev. B*, vol. 76, no. 3, p. 035420, Jul. 2007.
- [21] K. Okamoto, I. Niki, A. Scherer, Y. Narukawa, T. Mukai, and Y. Kawakami, "Surface plasmon enhanced spontaneous emission rate of InGaN /GaN quantum wells probed by time-resolved photoluminescence spectroscopy," *Appl. Phys. Lett.*, vol. 87, no. 7, p. 071102, Aug. 2005.
- [22] C. W. Lai, J. An, and H. C. Ong, "Surface-plasmon-mediated emission from metal-capped ZnO thin films," *Appl. Phys. Lett.*, vol. 86, no. 2, p. 251105, Jun. 2005.
- [23] J. Vuckovic, M. Loncar, and A. Scherer, "Surface plasmon enhanced light-emitting diode," *IEEE J. Quantum Electron.*, vol. 36, no. 10, pp. 1131–1144, Oct. 2000.
- [24] B. Guha, C. Otey, C. B. Poitras, S. Fan, and M. Lipson, "Near-field radiative cooling of nanostructures," *Nano Lett.*, vol. 12, pp. 4546–4550, Sep. 2012.
- [25] R. St-Gelais, B. Guha, L. Zhu, S. Fan, and M. Lipson, "Demonstration of strong near-field radiative heat transfer between integrated nanostructures," *Nano Lett.*, vol. 14, no. 12, pp. 6971–6975, Dec. 2014.
- [26] R. S. Ottens, V. Quetschke, S. Wise, A. A. Alemi, R. Lundock, G. Mueller, D. H. Reitze, D. B. Tanner, and B. F. Whiting, "Near-field radiative heat transfer between macroscopic planar surfaces," *Phys. Rev. Lett.*, vol. 107, no. 1, p. 014301, Jul. 2011.
- [27] K. E. and H. Raether, "Radiative decay of non radiative surface plasmons excited by light," *Zeitschrift für Naturforschung A*, vol. 23, no. 12, pp. 2135–&, 1968.
- [28] A. Otto, "Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection," *Zeitschrift für Physik*, vol. 216, pp. 398–410, 1968.
- [29] A. V. Zayats, I. I. Smolyaninov, and A. A. Maradudin, "Nano-optics of surface plasmon polaritons," *Phys. Rep.*, vol. 408, no. 3, pp. 131–314, Mar. 2005.
- [30] B. Liederg, C. Nylander, and I. Lundstrom, "Surface plasmon resonance for gas detectino and biosensing," *Sens. Actuators*, vol. 4, pp. 299–304, Aug. 1983.
- [31] B. Johnsson, S. Löfås, and G. Lindquist, "Immobilization of proteins to a carboxymethyldextran-modified gold surface for biospecific interaction analysis in surface plasmon resonance sensors," *Anal. Biochem.*, vol. 198, no. 2, pp. 268–277, Nov. 1991.
- [32] J. Melendez, R. Carr, C. Furlong, and R. Woodbury, "A commercial solution for surface plasmon sensing," *Sens. Actuators, B*, vol. 35, pp. 212–216, Apr. 1996.
- [33] J. Homola, I. Koudela, and S. S. Yee, "Surface plasmon resonance sensors based on diffraction gratings and prism couplers: sensitivity comparison," *Sens. Actuators, B*, vol. 54, pp. 16–24, Feb. 1999.
- [34] C. F. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles*. John Wiley & Sons, 2008.
- [35] M. Wright and A. Uddin, "Organic-inorganic hybrid solar cells: A comparative review," *Sol. Energy Mater. Sol. Cells*, vol. 107, no. C, pp. 87–111, Dec. 2012.
- [36] Z. Liu, J. Li, and F. Yan, "Package-free flexible organic solar cells with graphene top

- electrodes,” *Adv. Mater.*, vol. 25, no. 31, pp. 4296–4301, 2013.
- [37] S. Savagatrup, E. Chan, S. M. Renteria-Garcia, A. D. Printz, A. V. Zaretski, T. F. O'Connor, D. Rodriguez, E. Valle, and D. J. Lipomi, “Plasticization of PEDOT:PSS by common additives for mechanically robust organic solar cells and wearable sensors,” *Adv. Funct. Mater.*, vol. 25, no. 3, pp. 427–436, Nov. 2014.
- [38] C. Deibel and V. Dyakonov, “Polymer-fullerene bulk heterojunction solar cells,” *Rep. Prog. Phys.*, vol. 73, no. 9, p. 096401, Sep. 2010.
- [39] S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, and A. J. Heeger, “Bulk heterojunction solar cells with internal quantum efficiency approaching 100%,” *Nat. Photonics*, vol. 3, no. 5, pp. 297–302, May 2009.
- [40] J. Yang, J. You, C.-C. Chen, W.-C. Hsu, H.-R. Tan, X. W. Zhang, Z. Hong, and Y. Yang, “Plasmonic polymer tandem solar cell,” *ACS Nano*, vol. 5, no. 8, pp. 6210–6217, Aug. 2011.
- [41] D. Duche, P. Torchio, L. Escoubas, F. Monestier, J.-J. Simon, F. Flory, and G. Mathian, “Improving light absorption in organic solar cells by plasmonic contribution,” *Sol. Energy Mater. Sol. Cells*, vol. 93, no. 8, pp. 1377–1382, Aug. 2009.
- [42] C. Min, J. Li, G. Veronis, J.-Y. Lee, S. Fan, and P. Peumans, “Enhancement of optical absorption in thin-film organic solar cells through the excitation of plasmonic modes in metallic gratings,” *Appl. Phys. Lett.*, vol. 96, no. 1, p. 133302, Mar. 2010.
- [43] K. Q. Le, A. Abass, B. Maes, P. Bienstman, and A. Alu, “Comparing plasmonic and dielectric gratings for absorption enhancement in thin-film organic solar cells,” *Opt. Express*, vol. 20, no. 1, pp. A39–A50, Nov. 2011.
- [44] P. Zilio, D. Sammito, G. Zacco, M. Mazzeo, G. Gigli, and F. Romanato, “Light absorption enhancement in heterostructure organic solar cells through the integration of 1-D plasmonic gratings,” *Opt. Express*, vol. 20, no. 14, pp. A476–A488, 2012.
- [45] M. Akin Sefunc, A. Kemal Okyay, and H. V. Demir, “Plasmonic backcontact grating for P3HT:PCBM organic solar cells enabling strong optical absorption increased in all polarizations,” *Opt. Express*, vol. 19, no. 1, pp. 14200–14209, Jul. 2011.
- [46] W. Bai, Q. Gan, G. Song, L. Chen, Z. Kafafi, and F. Bartoli, “Broadband short-range surface plasmon structures for absorption enhancement in organic photovoltaics,” *Opt. Express*, vol. 18, no. 23, pp. A620–A630, 2010.
- [47] H. Shen and B. Maes, “Combined plasmonic gratings in organic solar cells,” *Opt. Express*, vol. 19, no. 23, pp. A1202–A1210, 2011.
- [48] X. Li, W. C. H. Choy, L. Huo, F. Xie, W. E. I. Sha, B. Ding, X. Guo, Y. Li, J. Hou, J. You, and Y. Yang, “Dual plasmonic nanostructures for high performance inverted organic solar cells,” *Adv. Mater.*, vol. 24, no. 22, pp. 3046–3052, Jun. 2012.
- [49] A. Christ, S. G. Tikhodeev, N. A. Gippius, J. Kuhl, and H. Giessen, “Waveguide-plasmon polaritons: strong coupling of photonic and electronic resonances in a metallic photonic crystal slab,” *Phys. Rev. Lett.*, vol. 91, no. 1, p. 183901, Oct. 2003.
- [50] S. Cho, J. H. Seo, S. H. Park, S. Beaupré, M. Leclerc, and A. J. Heeger, “A thermally stable semiconducting polymer,” *Adv. Mater.*, vol. 22, no. 11, pp. 1253–1257, Mar. 2010.
- [51] T.-Y. Chu, S. Alem, P. G. Verly, S. Wakim, J. Lu, Y. Tao, S. Beaupré, M. Leclerc, F. Bélanger, D. Désilets, S. Rodman, D. Waller, and R. Gaudiana, “Highly efficient polycarbazole-based organic photovoltaic devices,” *Appl. Phys. Lett.*, vol. 95, no. 6, p. 063304, 2009.

- [52] L. F. Johnson, H. J. Guggenheim, T. C. Rich, and F. W. Ostermayer, "Infrared-to-visible conversion by rare-earth ions in crystals," *J. Appl. Phys.*, vol. 43, no. 3, pp. 1125–1137, Mar. 1972.
- [53] V. E. Ferry, L. A. Sweatlock, D. Pacifici, and H. A. Atwater, "Plasmonic nanostructure design for efficient light coupling into solar cells," *Nano Lett.*, vol. 8, no. 12, pp. 4391–4397, Dec. 2008.
- [54] T. Holmgaard and S. Bozhevolnyi, "Theoretical analysis of dielectric-loaded surface plasmon-polariton waveguides," *Phys. Rev. B*, vol. 75, no. 24, p. 245405, Jun. 2007.
- [55] W. Chen, K. P. Chen, M. D. Thoreson, A. V. Kildishev, and V. M. Shalae, "Ultrathin, ultrasmooth, and low-loss silver films via wetting and annealing," *Appl. Phys. Lett.*, vol. 97, no. 2, p. 211107, Nov. 2010.
- [56] P. B. Johnson and R. W. Christy, "Optical constants of the noble metals," *Phys. Rev. B*, vol. 6, no. 12, p. 4370, 1972.
- [57] A. Raman, Z. Yu, and S. Fan, "Dielectric nanostructures for broadband light trapping in organic solar cells," *Opt. Express*, vol. 19, no. 20, pp. 19015–19026, 2011.
- [58] F. Auzel, "Upconversion and anti-Stokes processes with f and d ions in solids," *Chem. Rev.*, vol. 104, no. 1, pp. 139–173, Jan. 2004.
- [59] X. Huang, S. Han, W. Huang, and X. Liu, "Enhancing solar cell efficiency: the search for luminescent materials as spectral converters," *Chem. Soc. Rev.*, vol. 42, no. 1, pp. 173–201, 2013.
- [60] S. Sivakumar, F. C. J. M. van Veggel, and M. Raudsepp, "Bright white light through up-conversion of a single NIR source from sol-gel-derived thin film made with Ln^{3+} -doped LaF_3 nanoparticles," *J. Am. Chem. Soc.*, vol. 127, no. 36, pp. 12464–12465, Sep. 2005.
- [61] F. Wang, Y. Han, C. S. Lim, Y. Lu, J. Wang, J. Xu, H. Chen, C. Zhang, M. Hong, and X. Liu, "Simultaneous phase and size control of upconversion nanocrystals through lanthanide doping," *Nature*, vol. 463, no. 7284, pp. 1061–1065, Feb. 2010.
- [62] G. Chen, H. Qiu, P. N. Prasad, and X. Chen, "Upconversion nanoparticles: design, nanochemistry, and applications in theranostics," *Chem. Rev.*, vol. 114, no. 10, pp. 5161–5214, May 2014.
- [63] J. Zhou, Z. Liu, and F. Li, "Upconversion nanophosphors for small-animal imaging," *Chem. Soc. Rev.*, vol. 41, no. 3, pp. 1323–1349, 2012.
- [64] Q. Liu, W. Feng, T. Yang, T. Yi, and F. Li, "Upconversion luminescence imaging of cells and small animals," *Nat. Protoc.*, vol. 8, no. 10, pp. 2033–2044, Oct. 2013.
- [65] J. Zhao, D. Jin, E. P. Schartner, Y. Lu, Y. Liu, A. V. Zvyagin, L. Zhang, J. M. Dawes, P. Xi, J. A. Piper, E. M. Goldys, and T. M. Monro, "Single-nanocrystal sensitivity achieved by enhanced upconversion luminescence," *Nat. Nanotechnol.*, vol. 8, no. 10, pp. 729–734, Oct. 2013.
- [66] L. Wang, H. Dong, Y. Li, C. Xue, L.-D. Sun, C.-H. Yan, and Q. Li, "Reversible near-infrared light directed reflection in a self-organized helical superstructure loaded with upconversion nanoparticles," *J. Am. Chem. Soc.*, vol. 136, no. 12, pp. 4480–4483, Mar. 2014.
- [67] J. C. Goldschmidt and S. Fischer, "Upconversion for photovoltaics - a review of materials, devices and concepts for performance enhancement," *Adv. Opt. Mater.*, vol. 3, no. 4, pp. 510–535, Apr. 2015.
- [68] S. Fischer, E. Favilla, M. Tonelli, and J. C. Goldschmidt, "Record efficient

- upconverter solar cell devices with optimized bifacial silicon solar cells and monocrystalline $\text{BaY}_2\text{F}_8\text{:30\% Er}^{3+}$ upconverter,” *Sol. Energy Mater. Sol. Cells*, vol. 136, pp. 127–134, May 2015.
- [69] J. C. Goldschmidt, S. Fischer, P. Löper, K. W. Krämer, D. Biner, M. Hermle, and S. W. Glunz, “Experimental analysis of upconversion with both coherent monochromatic irradiation and broad spectrum illumination,” *Sol. Energy Mater. Sol. Cells*, vol. 95, no. 7, pp. 1960–1963, Jul. 2011.
- [70] R. H. Page, K. I. Schaffers, P. A. Waide, J. B. Tassano, S. A. Payne, W. F. Krupke, and W. K. Bischel, “Upconversion-pumped luminescence efficiency of rare-earth-doped hosts sensitized with trivalent ytterbium,” *J. Opt. Soc. Am. B*, vol. 15, no. 3, pp. 996–1008, Mar. 1998.
- [71] A. A. D. Adikaari, I. Etchart, P.-H. Guéring, M. Bérard, S. R. P. Silva, A. K. Cheetham, and R. J. Curry, “Near infrared up-conversion in organic photovoltaic devices using an efficient $\text{Yb}^{3+}\text{:Ho}^{3+}$ Co-doped $\text{Ln}_2\text{BaZnO}_5$ ($\text{Ln} = \text{Y, Gd}$) phosphor,” *J. Appl. Phys.*, vol. 111, no. 9, p. 4502, May 2012.
- [72] Q.-C. Sun, H. Mundoor, J. C. Ribot, V. Singh, I. I. Smalyukh, and P. Nagpal, “Plasmon-enhanced energy transfer for improved upconversion of infrared radiation in doped-lanthanide nanocrystals,” *Nano Lett.*, vol. 14, no. 1, pp. 101–106, Jan. 2014.
- [73] undefined author, W. Zhang, F. Ding, undefined author, and S. Y. Chou, “Large enhancement of upconversion luminescence of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ nanocrystal by 3D plasmonic nano-antennas,” *Adv. Mater.*, vol. 24, no. 35, pp. OP236–OP241, Sep. 2012.
- [74] E. Verhagen, L. Kuipers, and A. Polman, “Field enhancement in metallic subwavelength aperture arrays probed by erbium upconversion luminescence,” *Opt. Express*, vol. 17, p. 14586, Aug. 2009.
- [75] S. Schietinger, T. Aichele, H.-Q. Wang, T. Nann, and O. Benson, “Plasmon-enhanced upconversion in single $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ codoped nanocrystals,” *Nano Lett.*, vol. 10, no. 1, pp. 134–138, Jan. 2010.
- [76] D. M. Wu, A. García-Etxarri, A. Salleo, and J. A. Dionne, “Plasmon-enhanced upconversion,” *J. Phys. Chem. Lett.*, vol. 5, no. 22, pp. 4020–4031, Nov. 2014.
- [77] V. P. Drachev, U. K. Chettiar, A. V. Kildishev, H.-K. Yuan, W. Cai, and V. M. Shalaev, “The Ag dielectric function in plasmonic metamaterials,” *Opt. Express*, vol. 16, no. 2, pp. 1186–1195, 2008.
- [78] Z. Li and Y. Zhang, “An efficient and user-friendly method for the synthesis of hexagonal-phase $\text{NaYF}_4\text{:Yb, Er/Tm}$ nanocrystals with controllable shape and upconversion fluorescence,” *Nanotechnology*, vol. 19, no. 34, p. 345606, Jul. 2008.
- [79] J. D. Kingsley, “Analysis of energy transfer and infrared-to-visible conversion in $\text{LaF}_3\text{:Yb, Er}$,” *J. Appl. Phys.*, vol. 41, no. 1, pp. 175–182, 1970.
- [80] Y. Mita, “Luminescence processes in Yb^{3+} -sensitized rare-earth phosphors,” *J. Appl. Phys.*, vol. 43, no. 4, pp. 1772–1778, 1972.
- [81] J. C. Wright, “Up-conversion and excited state energy transfer in rare-earth doped materials,” in *Radiationless processes in molecules and condensed phases*, vol. 15, no. 4, Berlin, Heidelberg: Springer Berlin Heidelberg, 1976, pp. 239–295.
- [82] H.-X. Mai, Y.-W. Zhang, L.-D. Sun, and C.-H. Yan, “Highly efficient multicolor up-conversion emissions and their mechanisms of monodisperse $\text{NaYF}_4\text{:Yb,Er}$ core and core/shell-structured nanocrystals,” *J. Phys. Chem. C*, vol. 111, no. 37, pp. 13721–

- 13729, Sep. 2007.
- [83] Y. Xiaoqiang, C. J. Summers, and W. Park, "Controlling energy transfer processes and engineering luminescence efficiencies with low dimensional doping," *J. Appl. Phys.*, vol. 111, no. 7, p. 3524, Apr. 2012.
 - [84] B. Dong, B. Cao, Z. Feng, X. Wang, C. Li, and R. Hua, "Up-conversion emissions of Er^{3+} - Yb^{3+} codoped Al_2O_3 nanoparticles by the arc discharge synthesis method," *Sci. China, Ser. G: Phys., Mech. Astron.*, vol. 52, no. 7, pp. 1043–1046, Jul. 2009.
 - [85] C. Strohhofer and A. Polman, "Relationship between gain and Yb^{3+} concentration in Er^{3+} - Yb^{3+} doped waveguide amplifiers," *J. Appl. Phys.*, vol. 90, no. 9, p. 4314, 2001.
 - [86] J. Suyver, A. Aebischer, S. García-Revilla, P. Gerner, and H. Güdel, "Anomalous power dependence of sensitized upconversion luminescence," *Phys. Rev. B*, vol. 71, no. 12, p. 125123, Mar. 2005.
 - [87] G.-S. Yi and G.-M. Chow, "Water-soluble $\text{NaYF}_4\text{:Yb,Er(Tm)/NaYF}_4$ /polymer core/shell/shell nanoparticles with significant enhancement of upconversion fluorescence," *Chem. Mater.*, vol. 19, no. 3, pp. 341–343, Feb. 2007.
 - [88] Y. Ding, X. Zhang, H. Gao, S. Xu, C. Wei, and Y. Zhao, "Plasmonic enhanced upconversion luminescence of $\beta\text{-NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ with Ag@SiO_2 core-shell nanoparticles," *J. Lumin.*, vol. 147, pp. 72–76, Mar. 2014.
 - [89] J. D. Kingsley, G. E. Fenner, and S. V. Galginitis, "Kinetics and efficiency of infrared-to visible conversion in $\text{LaF}_3\text{:Yb,Er}$," *Appl. Phys. Lett.*, vol. 15, no. 4, pp. 115–117, Aug. 1969.
 - [90] J. Sommerdijk, "On the excitation mechanisms of the infrared-excited visible luminescence in Yb^{3+} , Er^{3+} -doped fluorides," *J. Lumin.*, vol. 4, pp. 441–449, Dec. 1971.
 - [91] D. Chen, Y. Wang, E. Ma, Y. Yu, and F. Liu, "Partition, luminescence and energy transfer of $\text{Er}^{3+}/\text{Yb}^{3+}$ ions in oxyfluoride glass ceramic containing CaF_2 nano-crystals," *Opt. Mater.*, vol. 29, no. 12, pp. 1693–1699, Aug. 2007.
 - [92] C. Florea and K. A. Winick, "Ytterbium-doped glass waveguide laser fabricated by ion exchange," *J. Lightwave Technol.*, vol. 17, no. 9, pp. 1593–1601, Sep. 1999.
 - [93] S. Taccheo, G. Sorbello, S. Longhi, and P. Laporta, "Measurement of the energy transfer and upconversion constants in Er - Yb -doped phosphate glass," *Opt. Quantum Electron.*, vol. 31, no. 3, pp. 249–262, Mar. 1999.
 - [94] K. A. Winick and G. L. Vossler, "Erbium: ytterbium planar waveguide laser in ion-exchanged glass," *SPIE proceedings series*, pp. 121–134, 1997.
 - [95] M. A. Chamarro and R. Cases, "Infrared to visible upconversion of Er^{3+} ions in Yb^{3+} doped fluorohafnate glasses," *J. Lumin.*, vol. 46, no. 1, pp. 59–65, 1990.
 - [96] D. C. Yeh, W. A. Sibley, M. Suscavage, and M. G. Drexhage, "Multiphonon relaxation and infrared-to-visible conversion of Er^{3+} and Yb^{3+} ions in barium-thorium fluoride glass," *J. Appl. Phys.*, vol. 62, no. 1, pp. 266–275, 1987.
 - [97] B. Simondi-Teisseire, B. Viana, D. Vivien, and A. M. Lejus, " Yb^{3+} to Er^{3+} energy transfer and rate-equations formalism in the eye safe laser material $\text{Yb:Er:Ca}_2\text{Al}_2\text{SiO}_7$," *Opt. Mater.*, vol. 6, no. 4, pp. 267–274, Nov. 1996.
 - [98] L. D. Deloach, S. A. Payne, L. L. Chase, D. R. Smith, W. L. Kway, and W. F. Krupke, "Evaluation of absorption and emission properties of Yb^{3+} doped crystals for laser applications," *IEEE J. Quantum Electron.*, vol. 29, no. 4, pp. 1179–1191, Apr. 1993.
 - [99] R. Esteban, M. Laroche, and J. J. Greffet, "Influence of metallic nanoparticles on

- upconversion processes,” *J. Appl. Phys.*, vol. 105, no. 3, p. 3107, Feb. 2009.
- [100] J. Nilsson, P. Scheer, and B. Jaskorzynska, “Modeling and optimization of short Yb^{3+} -sensitized Er^{3+} -doped fiber amplifiers,” *IEEE Photonics Technol. Lett.*, vol. 6, pp. 383–385, Mar. 1994.
 - [101] B.-C. Hwang, S. Jiang, T. Luo, J. Watson, G. Sorbello, and N. Peyghambarian, “Cooperative upconversion and energy transfer of new high Er^{3+} - and Yb^{3+} - Er^{3+} -doped phosphate glasses,” *J. Opt. Soc. Am. B*, vol. 17, no. 5, pp. 833–839, May 2000.
 - [102] J. Zhao, Z. Lu, Y. Yin, C. McRae, J. A. Piper, J. M. Dawes, D. Jin, and E. M. Goldys, “Upconversion luminescence with tunable lifetime in $\text{NaYF}_4\text{:Yb,Er}$ nanocrystals: role of nanocrystal size,” *Nanoscale*, vol. 5, no. 3, p. 944, 2013.
 - [103] C. Wyss, W. Lüthy, H. P. Weber, P. Rogin, and J. Hulliger, “Energy transfer in $\text{Yb}^{3+}\text{:YLF}$,” *Opt. Commun.*, vol. 144, no. 1, pp. 31–35, 1997.
 - [104] E. Cantelar, J. A. Muñoz, J. A. Sanz-García, and F. Cusso, “ Yb^{3+} to Er^{3+} energy transfer in LiNbO_3 ,” *J. Phys.: Condens. Matter*, vol. 10, no. 3, pp. 8893–8903, Oct. 1998.
 - [105] E. Cantelar and F. Cusso, “Dynamics of the Yb^{3+} to Er^{3+} energy transfer in LiNbO_3 ,” *Appl. Phys. B: Lasers Opt.*, vol. 69, no. 1, pp. 29–33, 1999.
 - [106] H. Dung, L. Knöll, and D.-G. Welsch, “Intermolecular energy transfer in the presence of dispersing and absorbing media,” *Phys. Rev. A*, vol. 65, no. 4, p. 043813, Apr. 2002.
 - [107] J. A. Gonzaga-Galeana and J. R. Zurita-Sánchez, “A revisit of the Förster energy transfer near a metallic spherical nanoparticle: (1) Efficiency enhancement or reduction? (2) The control of the Förster radius of the unbounded medium. (3) The impact of the local density of states,” *J. Chem. Phys.*, vol. 139, no. 24, p. 244302, Dec. 2013.
 - [108] J. I. Gersten and A. Nitzan, “Accelerated energy transfer between molecules near a solid particle,” *Chem. Phys. Lett.*, vol. 104, no. 1, pp. 31–37, Jan. 1984.
 - [109] X. M. Hua, J. I. Gersten, and A. Nitzan, “Theory of energy transfer between molecules near solid state particles,” *J. Chem. Phys.*, vol. 83, no. 7, p. 3650, 1985.
 - [110] A. Govorov, J. Lee, and N. Kotov, “Theory of plasmon-enhanced Förster energy transfer in optically excited semiconductor and metal nanoparticles,” *Phys. Rev. B*, vol. 76, no. 12, p. 125308, Sep. 2007.
 - [111] P. Andrew and W. L. Barnes, “Förster energy transfer in an optical microcavity,” *Science*, vol. 290, no. 5, pp. 785–788, Oct. 2000.
 - [112] M. Lunz, X. Zhang, V. A. Gerard, Y. K. Gun’ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, and A. L. Bradley, “Effect of metal nanoparticle concentration on localized surface plasmon mediated Förster resonant energy transfer,” *J. Phys. Chem. C*, vol. 116, no. 50, pp. 26529–26534, Dec. 2012.
 - [113] L. Novotny and B. Hecht, *Principles of Nano-Optics*. Cambridge University Press, 2012.
 - [114] M. de Dood, J. Knoester, A. Tip, and A. Polman, “Förster transfer and the local optical density of states in erbium-doped silica,” *Phys. Rev. B*, vol. 71, no. 11, p. 115102, Mar. 2005.
 - [115] C. Blum, N. Zijlstra, A. Lagendijk, M. Wubs, A. P. Mosk, V. Subramaniam, and W. L. Vos, “Nanophotonic control of the Förster resonance energy transfer efficiency,” *Phys. Rev. Lett.*, vol. 109, no. 20, p. 203601, Nov. 2012.
 - [116] P. Andrew and W. L. Barnes, “Energy transfer across a metal film mediated by surface

- plasmon polaritons,” *Science*, vol. 306, no. 5698, pp. 1002–1005, Nov. 2004.
- [117] Z.-K. Zhou, M. Li, Z.-J. Yang, X.-N. Peng, X.-R. Su, Z.-S. Zhang, J.-B. Li, N.-C. Kim, X.-F. Yu, L. Zhou, Z.-H. Hao, and Q.-Q. Wang, “Plasmon-mediated radiative energy transfer across a silver nanowire Array via resonant transmission and subwavelength imaging,” *ACS Nano*, vol. 4, no. 9, pp. 5003–5010, Sep. 2010.
 - [118] T. Nakamura, M. Fujii, S. Miura, M. Inui, and S. Hayashi, “Enhancement and suppression of energy transfer from Si nanocrystals to Er ions through a control of the photonic mode density,” *Phys. Rev. B*, vol. 74, no. 4, p. 045302, 2006.
 - [119] M. L. Viger, D. Brouard, and D. Boudreau, “Plasmon-enhanced resonance energy transfer from a conjugated polymer to fluorescent multilayer core–shell nanoparticles: a photophysical study,” vol. 115, no. 7, pp. 2974–2981, Feb. 2011.
 - [120] R. G. West and S. M. Sadeghi, “Enhancement of energy transfer between quantum dots: the impact of metallic nanoparticle sizes,” *J. Phys. Chem. C*, vol. 116, no. 38, pp. 20496–20503, Sep. 2012.
 - [121] X. Zhang, C. A. Marocico, M. Lunz, V. A. Gerard, Y. K. Gun’ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, and A. L. Bradley, “Experimental and theoretical investigation of the distance dependence of localized surface plasmon coupled Förster resonance energy transfer,” *ACS Nano*, vol. 8, no. 2, pp. 1273–1283, Feb. 2014.
 - [122] F. Th., “10th Spiers Memorial Lecture: Transfer mechanisms of electronic excitation,” *Discuss. Faraday Soc.*, vol. 27, p. 7, 1959.
 - [123] M. Inokuti and F. Hirayama, “Influence of energy transfer by the exchange mechanism on donor luminescence,” *J. Chem. Phys.*, vol. 43, no. 6, pp. 1978–1989, 1965.
 - [124] Z. Li, W. Park, G. Zorzetto, J. S. Lemaire, and C. J. Summers, “Synthesis protocols for δ -doped NaYF₄:Yb,Er,” *Chem. Mater.*, vol. 26, no. 5, pp. 1770–1778, Mar. 2014.
 - [125] H. Shpaisman, O. Niitsoo, I. Lubomirsky, and D. Cahen, “Can up- and down-conversion and multi-exciton generation improve photovoltaics?,” *Sol. Energy Mater. Sol. Cells*, vol. 92, no. 12, pp. 1541–1546, Dec. 2008.
 - [126] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, “Generation of optical harmonics,” *Phys. Rev. Lett.*, vol. 7, no. 4, pp. 118–119, Aug. 1961.
 - [127] J.-M. Gérard and B. Gayral, “Semiconductor microcavities, quantum boxes and the Purcell effect,” in *Lecture Notes in Physics*, vol. 531, no. 9, Springer Berlin Heidelberg, 1999, pp. 331–351.
 - [128] Y. Gong, J. Lu, S.-L. Cheng, Y. Nishi, and J. Vučković, “Plasmonic enhancement of emission from Si-nanocrystals,” *Appl. Phys. Lett.*, vol. 94, no. 1, p. 013106, 2009.
 - [129] A. F. Koenderink, “On the use of Purcell factors for plasmon antennas,” *Opt Lett*, vol. 35, no. 24, pp. 4208–4210, 2010.
 - [130] S. Coffa, G. Franzo, F. Priolo, A. Polman, and R. Serna, “Temperature dependence and quenching processes of the intra-4f luminescence of Er in crystalline Si,” *Phys. Rev. B*, 1994.
 - [131] M. Leroux, N. Grandjean, B. Beaumont, G. Nataf, F. Sémond, J. Massies, and P. Gibart, “Temperature quenching of photoluminescence intensities in undoped and doped GaN,” *J. Appl. Phys.*, vol. 86, no. 7, pp. 3721–3728, Oct. 1999.
 - [132] D. Li, Q. Shao, Y. Dong, and J. Jiang, “Anomalous temperature-dependent upconversion luminescence of small-sized NaYF₄:Yb³⁺,Er³⁺ nanoparticles,” *J. Phys. Chem. C*, vol. 118, no. 39, pp. 22807–22813, Oct. 2014.
 - [133] Y. Zhao, C. Riemersma, F. Pietra, R. Koole, C. de M. Donegá, and A. Meijerink,

- “High-temperature luminescence quenching of colloidal quantum dots.,” *ACS Nano*, vol. 6, no. 10, pp. 9058–9067, Oct. 2012.
- [134] W. Yu, W. Xu, H. Song, and S. Zhang, “Temperature-dependent upconversion luminescence and dynamics of $\text{NaYF}_4\text{:Yb}^{3+}/\text{Er}^{3+}$ nanocrystals: influence of particle size and crystalline phase.,” *Dalton Trans.*, vol. 43, no. 16, pp. 6139–6147, Apr. 2014.
- [135] S. Zhou, K. Deng, X. Wei, G. Jiang, C. Duan, Y. Chen, and M. Yin, “Upconversion luminescence of $\text{NaYF}_4\text{:Yb}^{3+},\text{Er}^{3+}$ for temperature sensing,” *Opt. Commun.*, vol. 291, pp. 138–142, Mar. 2013.
- [136] M. G. Nikolic, D. J. Jovanovic, and M. D. Dramicanin, “Temperature dependence of emission and lifetime in Eu^{3+} - and Dy^{3+} -doped GdVO_4 ,” *Appl. Opt.*, vol. 52, no. 8, pp. 1716–1724, 2013.
- [137] Y. Qi, Y. Zhou, L. Wu, F. Yang, S. Peng, S. Zheng, and D. Yin, “Enhanced upconversion emissions in $\text{Ho}^{3+}/\text{Yb}^{3+}$ codoped tellurite glasses containing silver NPs,” *J. Non-Cryst. Solids*, vol. 402, pp. 21–27, Oct. 2014.
- [138] P. Ghenuche, J. de Torres, S. B. Moparthi, V. Grigoriev, and J. Wenger, “Nanophotonic enhancement of the Förster resonance energy-transfer rate with single nanoapertures.,” *Nano Lett.*, vol. 14, no. 8, pp. 4707–4714, Aug. 2014.
- [139] Q. Lü, F. Guo, L. Sun, A. Li, and L. Zhao, “Silica/titania-coated $\text{Y}_2\text{O}_3\text{:Tm}^{3+},\text{Yb}^{3+}$ nanoparticles with improvement in upconversion luminescence induced by different thickness shells,” *J. Appl. Phys.*, vol. 103, no. 1, p. 3533, Jun. 2008.
- [140] G. Chen, H. Agren, T. Y. Ohulchanskyy, and P. N. Prasad, “Light upconverting core-shell nanostructures: nanophotonic control for emerging applications,” *Chem. Soc. Rev.*, Oct. 2014.
- [141] S. Han, R. Deng, X. Xie, and X. Liu, “Enhancing luminescence in lanthanide-doped upconversion nanoparticles,” *Angew. Chem. Int. Ed. Engl.*, vol. 53, no. 44, pp. 11702–11715, Oct. 2014.
- [142] H. Assaoudi, G.-B. Shan, N. Dyck, and G. P. Demopoulos, “Annealing-induced ultra-efficient NIR-to-VIS upconversion of nano-/micro-scale α and β $\text{NaYF}_4\text{:Er}^{3+},\text{Yb}^{3+}$ crystals,” *CrystEngComm*, vol. 15, no. 23, p. 4739, 2013.
- [143] J. Wang, R. Deng, M. A. MacDonald, B. Chen, J. Yuan, F. Wang, D. Chi, T. S. A. Hor, P. Zhang, G. Liu, Y. Han, and X. Liu, “Enhancing multiphoton upconversion through energy clustering at sublattice level,” *Nat. Mater.*, vol. 13, no. 2, pp. 157–162, Feb. 2014.
- [144] W. Zou, C. Visser, J. A. Maduro, M. S. Pshenichnikov, and J. C. Hummelen, “Broadband dye-sensitized upconversion of near-infrared light,” *Nat. Photonics*, vol. 6, no. 8, pp. 560–564, Jul. 2012.
- [145] T. U. Tumkur, J. K. Kitur, C. E. Bonner, A. N. Poddubny, E. E. Narimanov, and M. A. Noginov, “Control of Förster energy transfer in the vicinity of metallic surfaces and hyperbolic metamaterials,” *Faraday Discuss.*, vol. 178, pp. 395–412, 2015.
- [146] W. D. Newman, C. L. Cortes, D. Purschke, A. Afshar, Z. Chen, G. De los Reyes, F. Hegmann, K. Cadien, R. Fedosejevs, and Z. Jacob, “Super-Coulombic energy transfer: engineering dipole-dipole interactions with metamaterials,” presented at the CLEO: QELS_Fundamental Science, 2015, pp. FM3C–1.
- [147] J.-J. Greffet, R. Carminati, K. Joulain, J.-P. Mulet, S. Mainguy, and Y. Chen, “Coherent emission of light by thermal sources,” *Nature*, vol. 416, no. 6876, pp. 61–64, Mar. 2002.

- [148] M. Kreiter, J. Oster, R. Sambles, S. Herminghaus, S. Mittler-Neher, and W. Knoll, "Thermally induced emission of light from a metallic diffraction grating, mediated by surface plasmons," *Opt. Commun.*, vol. 168, no. 1, pp. 117–122, Sep. 1999.
- [149] O. Ilic, M. Jablan, J. D. Joannopoulos, I. Celanovic, and M. Soljačić, "Overcoming the black body limit in plasmonic and graphene near-field thermophotovoltaic systems," *Opt. Express*, vol. 20, no. 10, pp. A366–84, May 2012.
- [150] L. Hu, A. Narayanaswamy, X. Chen, and G. Chen, "Near-field thermal radiation between two closely spaced glass plates exceeding Planck's blackbody radiation law," *Appl. Phys. Lett.*, vol. 92, no. 13, p. 133106, 2008.
- [151] A. P. Raman, M. A. Anoma, L. Zhu, E. Rephaeli, and S. Fan, "Passive radiative cooling below ambient air temperature under direct sunlight," *Nature*, vol. 515, no. 7528, pp. 540–544, Nov. 2014.
- [152] B. J. Lee, Y. B. Chen, and Z. M. Zhang, "Confinement of infrared radiation to nanometer scales through metallic slit arrays," *J. Quant. Spectrosc. Radiat. Transfer*, vol. 109, pp. 608–619, Mar. 2008.
- [153] L. Wang, S. M. Uppuluri, E. X. Jin, and X. Xu, "Nanolithography using high transmission nanoscale bowtie apertures," *Nano Lett.*, vol. 6, no. 3, pp. 361–364, Mar. 2006.
- [154] Z.-W. Liu, Q.-H. Wei, and X. Zhang, "Surface plasmon interference nanolithography," *Nano Lett.*, vol. 5, pp. 957–961, May 2005.
- [155] Y. De Wilde, F. Formanek, R. Carminati, B. Gralak, P.-A. Lemoine, K. Joulain, J.-P. Mulet, Y. Chen, and J.-J. Greffet, "Thermal radiation scanning tunnelling microscopy," *Nature*, vol. 444, no. 7120, pp. 740–743, Dec. 2006.
- [156] M. Planck, *The Theory of heat radiation*. 1959.
- [157] K. Joulain, J.-P. Mulet, F. Marquier, R. Carminati, and J.-J. Greffet, "Surface electromagnetic waves thermally excited: Radiative heat transfer, coherence properties and Casimir forces revisited in the near field," *Surf. Sci. Rep.*, vol. 57, no. 3, pp. 59–112, May 2005.
- [158] A. C. Jones, B. T. O'Callahan, H. U. Yang, and M. B. Raschke, "The thermal near-field: Coherence, spectroscopy, heat-transfer, and optical forces," *Prog. Surf. Sci.*, vol. 88, no. 4, pp. 349–392, Dec. 2013.
- [159] J. B. Pendry, L. Martín-Moreno, and F. J. Garcia-Vidal, "Mimicking surface plasmons with structured surfaces," *Science*, vol. 305, no. 5685, pp. 847–848, Aug. 2004.
- [160] A. P. Hibbins, B. R. Evans, and J. R. Sambles, "Experimental verification of designer surface plasmons," *Science*, vol. 308, no. 5722, pp. 670–672, Apr. 2005.
- [161] F. J. Garcia-Vidal, L. Martín-Moreno, and J. B. Pendry, "Surfaces with holes in them: new plasmonic metamaterials," *J. Opt. A: Pure Appl. Opt.*, vol. 7, no. 2, p. 97, Feb. 2005.
- [162] G. Moddel and S. Grover, *Rectenna Solar Cells*. Springer, 2013.
- [163] Z. Zhu, S. Joshi, S. Grover, and G. Moddel, "Graphene geometric diodes for terahertz rectennas," *J. Phys. D: Appl. Phys.*, vol. 46, no. 1, p. 185101, May 2013.
- [164] Z. Zhu, S. Joshi, B. Pelz, and G. Moddel, "Overview of optical rectennas for solar energy harvesting," presented at the Proceedings of the SPIE, 2013, vol. 8824, p. 88240O.
- [165] S. A. Maier, *Plasmonics: Fundamentals and Applications*. Springer Science & Business Media, 2007.

- [166] H. P. Paudel, L. Zhong, K. Bayat, M. F. Baroughi, S. Smith, C. Lin, C. Jiang, M. T. Berry, and P. S. May, "Enhancement of Near-Infrared-to-Visible upconversion luminescence using engineered plasmonic gold surfaces," *J. Phys. Chem. C*, vol. 115, no. 39, pp. 19028–19036, Oct. 2011.
- [167] M. N. Gadalla, M. Abdel-Rahman, and A. Shamim, "Design, optimization and fabrication of a 28.3 THz nano-rectenna for infrared detection and rectification," *Sci. Rep.*, vol. 4, p. 4270, 2014.
- [168] Z. Han, Y. Zhang, and S. I. Bozhevolnyi, "Spoof surface plasmon-based stripe antennas with extreme field enhancement in the terahertz regime," *Opt Lett*, vol. 40, no. 11, pp. 2533–2536, Jun. 2015.
- [169] C. R. Otey, L. Zhu, S. Sandhu, and S. Fan, "Fluctuational electrodynamics calculations of near-field heat transfer in non-planar geometries: A brief overview," *J. Quant. Spectrosc. Radiat. Transfer*, vol. 132, no. C, pp. 3–11, Jan. 2014.
- [170] C. Luo, A. Narayanaswamy, G. Chen, and J. D. Joannopoulos, "Thermal radiation from photonic crystals: a direct calculation," *Phys. Rev. Lett.*, vol. 93, no. 21, p. 213905, Nov. 2004.
- [171] D. L. C. Chan, M. Soljačić, and J. D. Joannopoulos, "Direct calculation of thermal emission for three-dimensionally periodic photonic crystal slabs," *Phys. Rev. E*, vol. 74, no. 3, p. 036615, Sep. 2006.
- [172] S. M. Rytov, *Theory of Electric Fluctuations and Thermal Radiation*. Academy of Sciences Press, 1959.
- [173] A. Taflove, A. Oskooi, and S. G. Johnson, *Advances in FDTD Computational Electrodynamics*. Artech House, 2013.
- [174] M. G. Blaber, M. D. Arnold, and M. J. Ford, "Search for the ideal plasmonic nanoshell: the effects of surface scattering and alternatives to gold and silver," *J. Phys. Chem. C*, vol. 113, no. 8, pp. 3041–3045, Feb. 2009.
- [175] S. E. Han and D. J. Norris, "Beaming thermal emission from hot metallic bull's eyes," *Opt. Express*, vol. 18, p. 4829, Feb. 2010.
- [176] T. Inoue, M. De Zoysa, T. Asano, and S. Noda, "Realization of dynamic thermal emission control," *Nat. Mater.*, vol. 13, no. 10, pp. 928–931, Oct. 2014.
- [177] S. Molesky, C. J. Dewalt, and Z. Jacob, "High temperature epsilon-near-zero and epsilon-near-pole metamaterial emitters for thermophotovoltaics," *Opt. Express*, vol. 21, pp. A96–110, Jan. 2013.
- [178] J. Homola, "Present and future of surface plasmon resonance biosensors," *Anal. Bioanal. Chem.*, vol. 377, no. 3, pp. 528–539, Oct. 2003.
- [179] X. Huang, I. H. El-Sayed, W. Qian, and M. A. El-Sayed, "Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods," *J. Am. Chem. Soc.*, vol. 128, no. 6, pp. 2115–2120, Feb. 2006.
- [180] A. Campion and P. Kambhampati, "Surface-enhanced Raman scattering," *Chem. Soc. Rev.*, vol. 27, no. 4, p. 241, 1998.
- [181] J. N. Munday and H. A. Atwater, "Large integrated absorption enhancement in plasmonic solar cells by combining metallic gratings and antireflection coatings," *Nano Lett.*, vol. 11, no. 6, pp. 2195–2201, Jun. 2011.
- [182] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, "Surface plasmon enhanced silicon solar cells," *J. Appl. Phys.*, vol. 101, no. 9, p. 093105, 2007.
- [183] C. Ciraci, R. T. Hill, J. J. Mock, Y. Urzhumov, A. I. Fernández-Domínguez, S. A.

- Maier, J. B. Pendry, A. Chilkoti, and D. R. Smith, "Probing the ultimate limits of plasmonic enhancement," *Science*, vol. 337, no. 6098, pp. 1072–1074, Aug. 2012.
- [184] I. Diukman, L. Tzabari, N. Berkovitch, N. Tessler, and M. Orenstein, "Controlling absorption enhancement in organic photovoltaic cells by patterning Au nano disks within the active layer," *Opt. Express*, vol. 19, pp. A64–71, Jan. 2011.
- [185] A. Abass, H. Shen, P. Bienstman, and B. Maes, "Angle insensitive enhancement of organic solar cells using metallic gratings," *J. Appl. Phys.*, vol. 109, no. 2, p. 023111, 2011.
- [186] Q. Luu, A. Hor, J. Fisher, R. B. Anderson, S. Liu, T.-S. Luk, H. P. Paudel, M. Farrokh Baroughi, P. S. May, and S. Smith, "Two-color surface plasmon polariton enhanced upconversion in NaYF₄:Yb:Tm nanoparticles on Au nanopillar arrays," *J. Phys. Chem. C*, vol. 118, no. 6, pp. 3251–3257, Feb. 2014.
- [187] H. Zhang, D. Xu, Y. Huang, and X. Duan, "Highly spectral dependent enhancement of upconversion emission with sputtered gold island films," *Chem. Commun.*, vol. 47, no. 3, pp. 979–981, Jan. 2011.