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The Emission Enhancement around Spherical Plasmonic Particles

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Abstract

The spontaneous emission of a single emitter could be strongly affected by adjacent nano structures due to the Purcell effect. It is well known that a cavity with higher quality factor Q and smaller mode volume V can provide better performance according to Purcell, little effort has been paid to find the limitation of the enhancement. We, in this essay, provide a continuum and complete phase picture of enhancement varies from different Q and V both for photonic cavity and plasmonic cavity. Moreover, we give the detail analysis of radiation and non-radiation decay in plasmonic cavity to support our point of view. We believe this work will pave the way in high performance nano cavity manufacture.

Keywords

Purcell Factor; Plasmonic Cavity; Quenching; Density of States.

1. Introduction

The fluorescence of a single emitter can be strongly modified by its electromagnetic environment, a photonic cavity like Whispering-Gallery microsphere, or a metallic sphere near the emitter performing as a plasmonic cavity can act like an antenna, shorting the lifetime of the spontaneous emission. Plenty of attention has been focused on higher enhancement in spontaneous emission rate for the potential application in bio-sensing[1], quantum computing[2], single molecule laser[3], novel light matter interaction[4] and so on. Great progress has been achieved in both photonic cavity[5] and plasmonic cavity system[6], the enhancement of spontaneous emission rate has reached more than 1000 times, researchers keep focusing on increasing the quality factor Q and shrinking the mode volume V, following the guideline of Purcell given in 1946[7]. In this article, we will give a theoretical model combing both cavity systems, show the limitation of cavity enhancement and the underlie mechanism. The finding of our study can be the guideline in further cavity research.

Intuitively, considering the scale mismatch of the wavelength and the atom size, the electromagnetic field is nearly equal among the whole atom, therefore the interaction is relatively weak, and the absorption and spontaneous emission probability is relatively small. Theoretically, the transition rate between two energy state of an atom is given by Fermi golden rule, $\Gamma_{i\to j} = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2\rho(E_f)$. It is clear that the transition rate is dominated by the final energy density of state (DOS). For a single quantum emitter placed inside a resonance nanocavity, the local energy density of state will be confined. Therefore, the spontaneous emission rate will be strongly enhanced, this process is known as Purcell effect.

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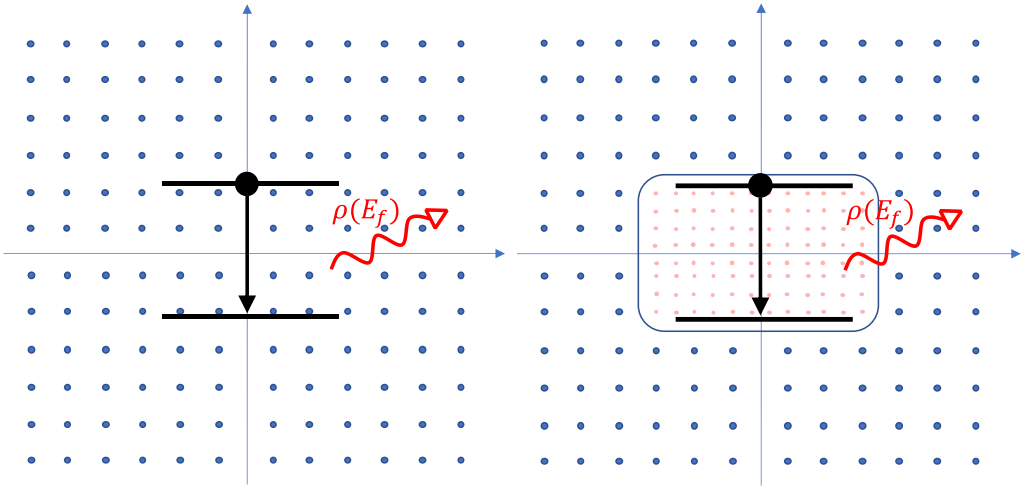

Fig. 1 The sketch of final energy density of state in free space (left) and inside the resonance nano cavity (right). The DOS inside the cavity is confined so that the transition rate from excited state to ground state is enhanced.

In 1946, Purcell published an article named spontaneous emission probabilities at radio frequency, in which he claimed that the spontaneous emission of an emitter at radio frequency could be strongly enhanced once it is coupled to a resonance electric circuit. Moreover, he gives the enhancement factor $F_p = \frac{3}{4\pi^2}\left(\frac{\lambda_{free}}{n}\right)^3 \frac{Q}{V}$, where λ_{free} is the wavelength of emission in free space, n is the reflex index of the QE environment, Q and V are the quality factor and mode volume of the cavity.

Quality factor Q represents the energy decay of the cavity, the general definition is the two pi multiplied by energy stored inside the cavity over energy decay every cycle. The higher the Q is, the more times a photon can travel inside the cavity, the more possible it can interact with the emitter, therefore, the local density of states inside the cavity enhance. Mode volume V represents how confined the cavity is, the smaller the cavity, the stronger the electromagnetic field.

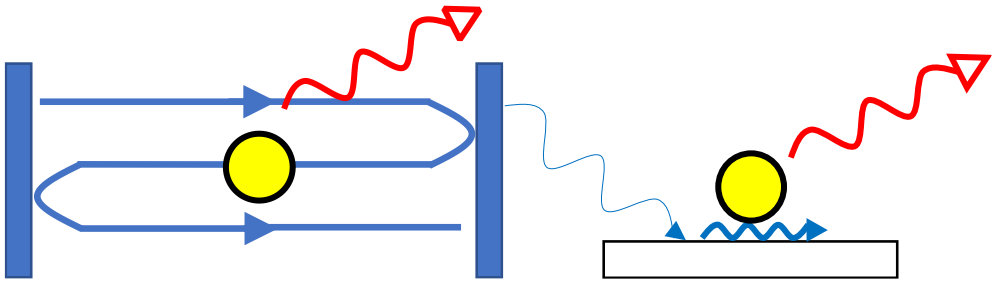

Fig. 2 Quality factor Q enhance the interaction time between the electromagnetic wave and the atom (left), and mode volume V enhance the optical field strength.

In the past decades, plenty of cavities have been create including Fabry-Perot cavity, whispering gallery cavity, photonic crystal cavity, metal sphere, bowtie cavity and so on[8-12]. There are separated into two main types according to their Q and V features. Photonic cavities are made of dielectric material, they have low optical loss, therefore, very high Q. however, because of the limitation of diffraction, the cavity mode volume V must be larger than $\left(\frac{\lambda}{2n}\right)^3$ or the photon cannot exist inside the cavity. Plasmonic cavities are made of metal, the existence of surface plasmon helps to shrink the light so that the plasmonic cavities can break the diffraction limit and have much smaller mode volume. The shortcoming is that the surface plasmon also brings high energy loss, and the quality factor of plasmonic cavity is restricted.

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2. Theoretical Models

There is an important concept we have to clear ahead, the emission we detect or observe in a cavity system experiment is not directly from the emitter itself. Considering the case that the emitter inside a cavity with quality factor approaching infinite, it will be a conserved system with very strong light and matter interactions inside, however, no matter how strong the interaction is, we would never detect any photon coming out of the cavity.

Fig3 shows the exact mechanism of an emitter-cavity system. The light-matter interaction is enhanced inside the cavity, the spontaneous emission rate is increasing, while what we observe is the leakage emission of the cavity γ_{cav}.

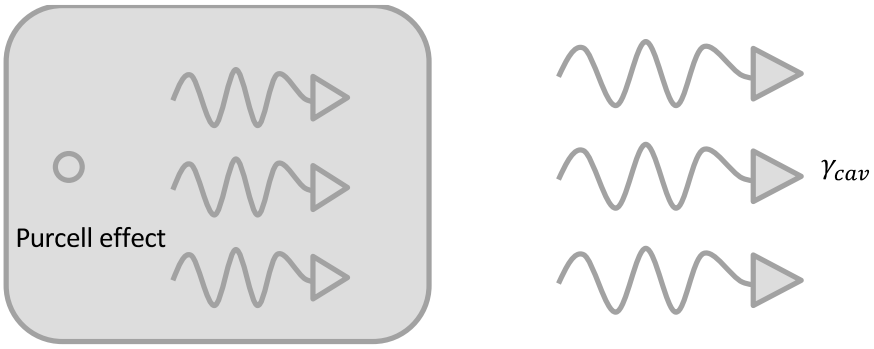

Fig. 3 A quantum emitter inside a resonance cavity, the light-matter interaction is enhanced. The emission coming out of the cavity is defined as γ_{cav}.

For photonic cavity, which is diffraction-limited, improving the Q is the only method to proceed the performance. Generally, photonic cavity has material loss Q_{mat}, surface scattering loss Q_s, radiation loss Q_r, but when the cavity size is at several hundred nanometers, the Q_r dominates because of the diffraction limit. It is reasonable to take all the energy loss of the cavity as γ_{cav} which gives us the up limitation as $\gamma_{cav} = \omega/Q$. ω is the resonance frequency of the cavity and Q is the quality factor. With an increasing Q, the transition rate inside the cavity is enhanced by the Purcell factor F_p so the emission rate should be $F_p\gamma_0$ where γ_0 is the spontaneous emission rate in free space, the cavity leakage rate is limited by $\gamma_{cav} = \omega/Q$ origins from the quality factor definition. Since the energy coming out of the cavity cannot exceed the cavity emission rate, the decreasing γ_{cav} will inevitably limit the total emission rate[13].

Intuitively, we can get the optimized situation when the transition rate $F_p\gamma_0$ is equal to the cavity leakage rate γ_{cav}, each photon formed by the transition inside the cavity leave the cavity just before the next transition happens and no waiting for either emitter or cavity. This optimized situation is also the boundary of the weak and strong coupling for the emitter-cavity system[14], in the weak coupling regime where $g_{coup} \ll \gamma_0, \gamma_{cav}$, the enhancement for transition with increasing Q will dominate the total emission rate, while in the strong coupling regime, $g_{coup} \gg \gamma_0, \gamma_{cav}$, the cavity leakage rate become the limitation and the photon will be stored inside the cavity, eventually reabsorbed by the emitter itself, this is called Rabi oscillation[4].

To have a better understanding of the process, we start with the classical two-level system with an energy conserved cavity, and we get a standard Rabi oscillation form, where x is the state with excited atom and no photon in cavity, y is the state with ground state atom and one photon in cavity, and $\Omega_R = F_p\gamma_0$ is the Rabi frequency.

$$\dot{x}(t) = \frac{i\Omega_R}{2} y(t)$$

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$$\dot{y}(t) = \frac{i\Omega_R}{2}x(t)$$

In a real case, we know the cavity cannot be without any energy dissipation, so we add one term in the second equation indicating that the state with ground state atom and one photon in cavity can release the photon at a rate of γ_{cav}, and we get,

$$\dot{x}(t) = \frac{i\Omega_R}{2}y(t)$$
$$\dot{y}(t) = \frac{i\Omega_R}{2}x(t) - \frac{\gamma_{cav}}{2}y(t)$$

Take the initial condition as $x(0) = 1, y(0) = 0$, we will get the solution:

$$x(t) = \frac{s_2 e^{s_1 t} - s_1 e^{s_2 t}}{s_2 - s_1}, \qquad y(t) = \frac{i\Omega_R}{2(s_1 - s_2)}(e^{s_1 t} - e^{s_2 t})$$

Where $s_{1,2}$ is defined as:

$$s_{1,2} = \frac{-\frac{\gamma_{cav}}{2} \mp \sqrt{(\frac{\gamma_{cav}}{2})^2 - {\Omega_R}^2}}{2}$$

And we can get the emission rate out of cavity as $r(t) = \gamma_{cav}|y(t)|^2$, our calculation shows that the out of cavity emission rate could be affect by both Q and V features. The mode volume V only relates to the coupling strength Ω_R, the quality factor Q, as mentioned above, also dominates the γ_{cav}. If we manipulate Q or V of the cavity, the consequences are not necessarily equivalent.

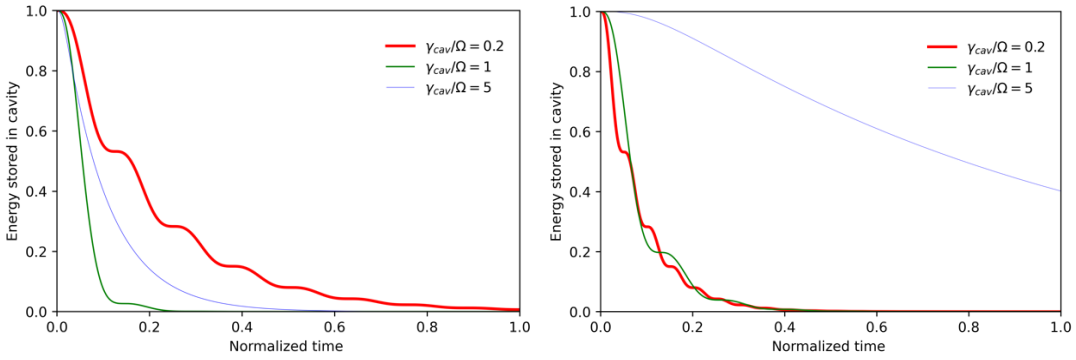

Fig. 4 The time evolution process of emitter-cavity system with initial condition$x(0) = 1, y(0) = 0$. Red thick curve represents the R=0.2, which is strong coupling regime, green curve represents the R=1, which is between the strong and weak coupling regime, thin blue curve represents the weak coupling regime. Left) this sketch shows the results of different R by manipulating the quality factor Q. Right) this sketch shows the results of different R by manipulating the mode volume V.

We use $R = \frac{\Omega_R}{\gamma_{cav}}$ as the parameter to draw the solution of different cavity, the left picture of Fig4 proves clearly that neither weak coupling nor strong coupling gives the best cavity, the optimized

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situation is when the emitter-cavity system reaches balance, we are not necessarily to reach enormous Q to find the best cavity because once the Q is over the balance, the emission will be trapped inside, starting Rabi oscillation and inhibiting the total emission. The meaning of right picture of Fig4 is to show that by shrinking the V of the cavity, even the system reaches strong coupling regime, the total emission will not be suppressed.

Let us now consider the plasmonic cavity system. Most of the mechanism is the same as the photonic cavity except two main differences, one is that the Q and V are not at the same scale because of the material properties, the other is that the cavity emission rate of plasmonic cavity is different[15]. In the photonic cavity part, we ignore some dissipation to get the $\gamma_{cav} = \omega/Q$ approximation, however, in plasmonic cavity, the energy decay due to the cavity is defined as $\gamma_{nr} + \gamma_r = \omega/Q$.

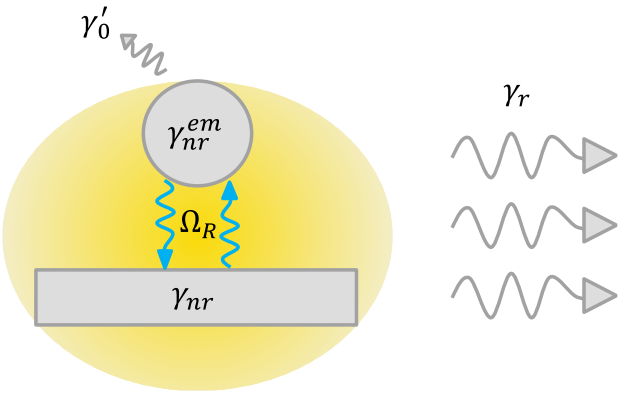

Fig. 5 The energy transfer for a plasmonic cavity system, $\gamma_0{}'$ is the emission of the emitter that is not coupling with the cavity, γ_{nr}^{em} is the nonradiative decay due to the emitter itself, Ω_R is the Rabi frequency, γ_{nr} and γ_r are the nonradiative and radiative cavity dissipation respectively.

At the beginning of this century, the consequences of the placing a metal nanostructure near a quantum emitter are not consistent. While some studies show fluorescence enhancement[16, 17], other studies report fluorescence inhibited[18, 19], we now get the mechanism of this confliction, when a quantum emitter is placed adjacent to metal, its interaction with electromagnetic field will be enhanced due to the confined optical field just like the photonic cavity, however, the strong absorption of metal will inhibit the emission[20]. For a plasmonic cavity system, we should make a modification when we are calculating the total emission rate, $r(t) = q_n \gamma_{cav} |y(t)|^2$. We add a factor q_n to represent the absorption, which is the quantum yield of the plasmonic cavity system, this is a concept that have rarely been used in cavity research area, we define $q_n = \frac{\gamma_r}{\gamma_{nr}+\gamma_r}$.

The mode volume V is generally defined as $V = \frac{\int \varepsilon(\vec{r})|\vec{E}(\vec{r})|^2 dV}{max\left(\varepsilon(\vec{r})|\vec{E}(\vec{r})|^2\right)}$, from the definition, we can get the one who raise the idea of mode volume wants to quantify how much the optical field is confined. Specific articles are published to discuss the details in plasmonic cavity mode volume[21], what we try to clarify here is that the definition gives us the maximum confinement of the optical filed inside cavity, we cannot use that in real case calculation. In a real experiment, the position of the quantum emitter is hardly to be the optimized position, therefore, we should use another parameter to replace the mode volume V.

Consider a quantum emitter placed in different position of the same plasmonic cavity, and we ignore the field difference changed by the emitter. We give the effective mode volume for the quantum emitter at $\vec{r_1}$ and $\vec{r_2}$ as $V_{r_1} = \frac{\int \varepsilon(\vec{r})|\vec{E}(\vec{r})|^2 dV}{\varepsilon(\vec{r_1})|\vec{E}(\vec{r_1})|^2}$ and $V_{r_2} = \frac{\int \varepsilon(\vec{r})|\vec{E}(\vec{r})|^2 dV}{\varepsilon(\vec{r_2})|\vec{E}(\vec{r_2})|^2}$ respectively. With the statement and the approximation given ahead, we can get the $\int \varepsilon(\vec{r})\left|\vec{E}(\vec{r})\right|^2 dV$ part for both V_{r_1} and V_{r_2} are

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equal, and the effective mode volume ratio can be simplified to $\frac{V_{r_1}}{V_{r_2}} = \frac{\varepsilon(\vec{r_2})|\vec{E}(\vec{r_2})|^2}{\varepsilon(\vec{r_1})|\vec{E}(\vec{r_1})|^2}$, and if the dielectric constant is uniform inside the cavity, we can finally get the conclusion $\frac{V_{r_1}}{V_{r_2}} = \frac{|\vec{E}(\vec{r_2})|^2}{|\vec{E}(\vec{r_1})|^2}$. We can plug this result back in the Purcell factor and get $\frac{P_{r_1}}{P_{r_2}} = \frac{|\vec{E}(\vec{r_1})|^2}{|\vec{E}(\vec{r_2})|^2}$, the enhancement of the Purcell effect inside a plasmonic cavity is proportional to the square of the optical field enhancement.

3. Simulation Results and Discussion

Intuitively, the optical field increase as the distance to the metal nanostructure decrease due to the surface plasmon, also, the absorption grows stronger as the distance decrease. The field enhancement leads to the transition rate enhancement, while the absorption dominates the q_n of the cavity. There is a competition between these two mechanisms, and both relate to the distance, so we are trying to get the underlie relation to give out a general simple conclusion.

We use COMSOL Multiphysics to simulate a plasmonic cavity system of a quantum emitter near a single gold nano sphere, focusing on the optical field enhancement around the nano sphere and the ratio of the absorption by the nanosphere and the far field emission.

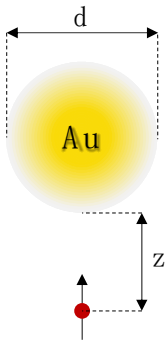

Fig. 6 Model plasmonic cavity used for COMSOL Multiphysics simulations, a gold sphere with diameter d and a single quantum emitter with vertical dipole moment. The distance between the emitter and the gold sphere is z.

The simulation model is given in Fig6, in this simulation, we first apply a vertical electromagnetic wave propagate from the top to the bottom to get the optical filed distribution around the sphere, which is related to the mode volume V as mentioned above. Then we use a dipole to simulate the quantum emitter, integrate the absorption of the metal and the far field emission to get the quantum yield q_n. With the enhancement of optical field and the quantum yield q_n, we can compute the total emission rate for plasmonic cavity $r(t) = q_n\gamma_{cav}|y(t)|^2$.

3.1 Influence of a Gold Sphere on the Local Electric Field Enhancement

Since the transition rate of an emitter can be strongly modified by the electromagnetic environment, we first study the local field distribution under planewave illumination using the above model. This is a very simple model and has been widely studied, the field distribution is not as complicated as the scanning tunneling microscope tip or bowtie nano structure[22], while the underlying mechanism can be easier to recognized.

Here the gold sphere is illuminated by a polarized plane wave with wavelength of 700nm and an amplitude of unit 1 propagating from the top to the bottom. As shown in Fig7, the gold sphere with radius 100nm is surrounded by a sphere of air with radius 600nm, and the whole physical domain is covered by 300nm perfect match layer (PML) to prevent all the reflection on the boundary. The gold reflex index parameter is given by Brendel-Bormann model. From the simulation result in Fig7(a),

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we can see that the electric fields are strongly localized near the sphere with the maximum electric field enhancement around 4. The local enhanced electric field indicates that the emission rate will be increased once an emitter is placed here, and the transition rate enhancement is proportional to the square of the electric field. We plot the electric field distribution from the top surface of the gold sphere to 100nm above, getting the relation of the electric field enhancement and the distance to the top surface in Fig7(b), the electric field decrease as the distance increase.

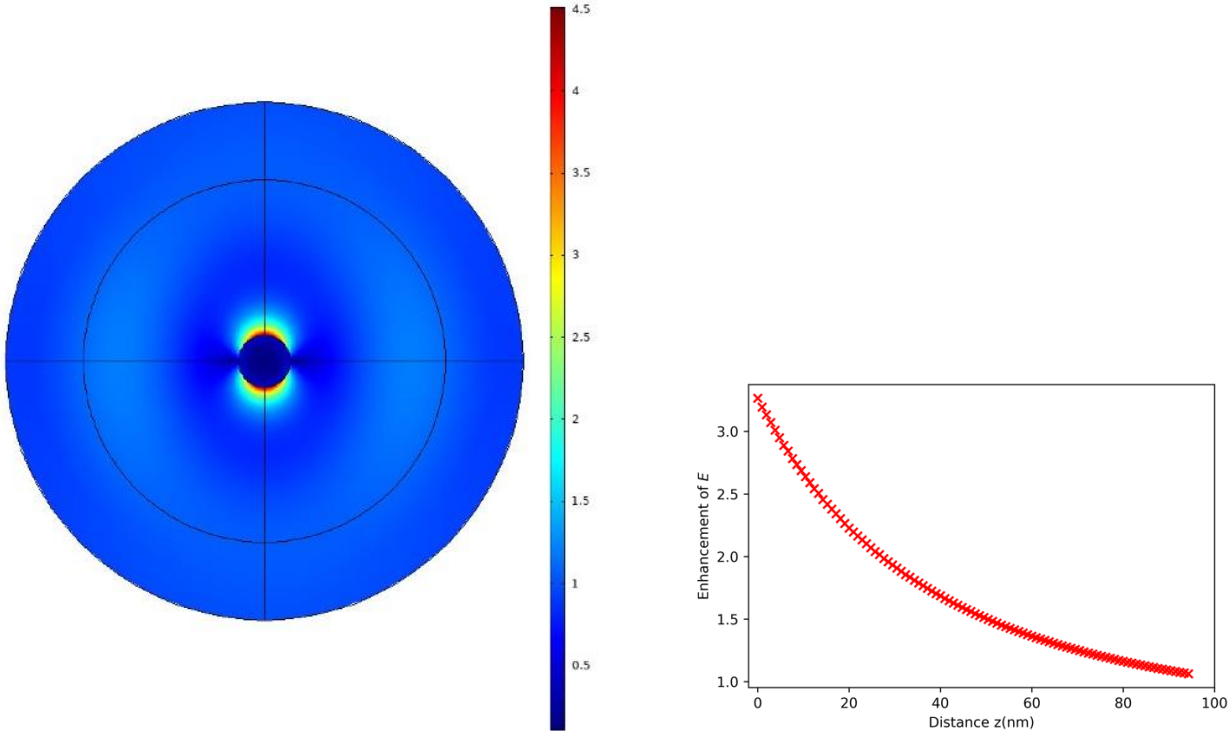

Fig. 7 The electric field distribution of the gold sphere, front view. (a) the field is confined near the gold sphere on the polarization direction. (b) the electric field as a function of distance from the top surface to 100nm above the gold sphere.

The next step is to find the relation of distance and q_n, we use nearly the same geometry model, the only difference is to use a point dipole as the energy source instead of the incident electromagnetic field. We place a dipole right above the gold sphere as the emitter and integrate the Poynting vector of the surface of physical domain (the whole model except the PML) to get the far field emission energy, or in other words, the radiation decay energy. Then we integrate the Poynting vector of the surface of gold sphere to get the absorption, which represents the nonradiative energy decay. Also, we integrate the energy absorption of the gold sphere domain, to verify the nonradiative decay, and we get the same numbers. The quantum yield of the cavity is then given by $q_n = \frac{emission}{absorption+emission}$. We change the distance of the dipole and the gold sphere and finally get the relation of q_n and distance. As shown in Fig8(a) we can see the electromagnetic waves are strongly confined near the gold sphere, and the far field emission is low. The Fig8(b) shows that the q_n decrease strongly as the emitter approaches the gold sphere, the absorption becomes enormous at short distance.

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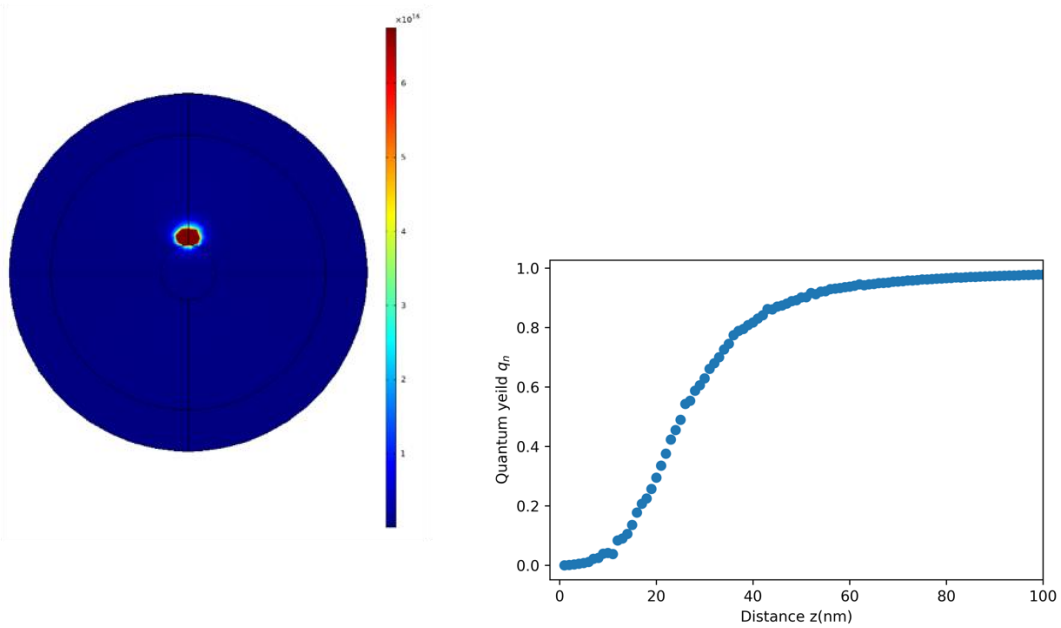

Fig. 8 The radiation distribution of emitter near the gold sphere. (a) the sketch of the emitter radiation. (b) the radiation ratio of the whole energy decay as a function of distance of emitter and gold sphere.

In Fig7(b) and Fig8(b), we see the enhancement and the inhibition distance dependences respectively, as mentioned above, we believe the total emission enhancement is the competition of these two mechanisms. We multiply the square of electric field enhancement and the quantum field to get the relation of total emission verse distance, the simulation result is consistent with the result given by Lukas Novotny[20], at short distance, the nonradiative decay due to the metal dominants, while at long distance, the affection of both enhancement and inhibition vanishes, at the middle distance, there exist an optimized distance that the field caused transition rate enhancement is stronger than the absorption due to the metal, and that is the best position for a plasmonic cavity, also the best mode volume for plasmonic cavity.

The underlie mechanisms of both cavities have been explained clearly, we then draw the map of spontaneous emission enhancement for both photonic cavity and plasmonic cavity with all Q and V using the formula given above.

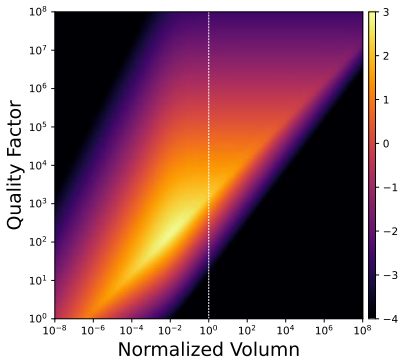

Fig. 9 The out of cavity spontaneous emission rate of the cavity system. The enhancement as a function of normalized mode volume and quality factor for both photonic cavity and plasmonic cavity.

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We can see clearly that the best photonic cavity located at the diffraction limit mode volume while plasmonic cavity does not have to be as small as we can manufacture and the quality factor of both cavities have optimized value. The map also shows that the spontaneous emission limitation of plasmonic cavity is two magnitudes bigger than the limitation of photonic cavity. The limitation happens when the transition rate of the quantum emitter inside cavity exceeds the speed which photon leaves the cavity

4. Conclusion

In this paper, we theoretically analyze the underlie mechanism of cavity-emitter system, discussing separately on photonic and plasmonic cavity due to their different material properties. We also use a numerical simulation to study the radiative and nonradiative decay of plasmonic cavity to figure out the competition of enhancement and inhibition in plasmonic cavity. In the end, we use the formula derived above to calculate the enhancement for all cavities, giving a map of the total spontaneous emission enhancement for both photonic cavity and the plasmonic cavity. We believe this work could be the guideline for further high-quality cavity manufacture.

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