Radiative Decay Rate Enhancement and Quenching for Multiple Emitters near a Metal Nanoparticle Surface

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ABSTRACT: When molecules (emitters) are placed near a metal surface, their Raman scattering will be significantly enhanced, and their fluorescence signal might be enhanced or quenched. Both these two phenomena are closely related to the enhancement of the radiative decay rate (RDR) of the molecules upon the presence of a nearby metal nanoparticle. Using a recently developed model, we found that the RDR enhancement or quenching for two or more emitters placed near a spherical Ag nanoparticle surface is drastically different from that when only one emitter is included. When three emitters are arranged near the metal surface, the overall enhancement factor can be even much smaller than the lowest enhancement factor of one emitter. If six emitters are evenly arranged near the metal surface, the enhancement factors at different wavelengths exhibit an asymmetric line shape near the resonance wavelength of metal nanoparticle and the line shape will converge when the number of emitters is increased further. When emitters are placed at different distances from the nanoparticle surface, the coupling between one emitter and the metal nanoparticle along the dipole axis exhibit near field characteristic while the enhancement factor of RDR for six emitters arranged evenly around a metal nanoparticle follows a far field trend. The discoveries will advance our fundamental understanding of the enhancement and quenching mechanism of emitters near metal nanoparticle surfaces, especially for those with high quantum yield which allows more than one of them to radiate simultaneously near one metal nanoparticle surface.

INTRODUCTION

When a molecule is placed near a metal nanoparticle surface, the optical properties of the molecule will be significantly affected by the nearby nanoparticle. The most noticeable change is the surface enhanced Raman scattering which have been extensively studied both experimentally and theoretically.[1-8] The enhancement factor of the Raman scattering near a spherical nanoparticle has been proposed to be proportional to the enhanced local electric field of the metal nanoparticle at both excitation and scattering wavelengths at the position of the molecule.[3] The theory has been proved to be a success in explaining many experimental measurements.[9,10] In 2015, Zhou et. al. numerically demonstrated that the enhancement factor of the Raman scattering at the scattering wavelength cannot be accurately predicted using the enhanced local electric field when a rod-shaped particle is used.[11] A direct calculation of the scattering cross section of an oscillating dipole with and without the presence of metal nanoparticle should be applied to accurately predict the enhancement factor of the scattering.[11] Khlebtsov et. al. [12] studied the enhancement factor of Raman scattering in a rod shaped particle using both experimental and theoretical approaches and observed discrepancy between the experimental observation and the theoretical prediction calculated using the enhanced local electric field model. Zhang et. al. theoretically studied the enhancement factors in a particle dimer and obtained the similar conclusion.[13]

The mechanism for the surface enhanced/quenched fluorescence,[14-17] on the other hand, is more complex than that of the surface enhanced Raman scattering. Scientists believe that the complication is mainly due to the larger quantum yield of the fluorophore in comparison to that of Raman scattering. In many of the previous theoretical models, one emitter was used to evaluate the enhancement factor of Raman scattering or the enhancement/quenching factor of

fluorescence signal. [3,8,18,19] There are also several studies on the enhanced and quenched emission for multiple emitters near metal nanoparticles. The studies revealed that the coupling among multiple emitters and metal nanoparticles is very different from that of one emitter.[20-23] In 1954, Robert Dicke[24] proposed coherence in spontaneous radiation processes. In the paper, Dicke pointed out that when atoms (emitters) are arranged with a distance much smaller than their radiation wavelength, the emission cannot be treated separately, and should be treated collectively as a super-radiant state. Super-radiance of self-assembled quantum dots has been experimentally reported.[25] There have been several theoretical studies of Dicke effects for an ensemble of emitters near metal nanoparticles.[20-23] Shahbazyan et al.[20] investigated the plasmonic Dicke effect. They arranged dipoles in CN configuration where N=20, 32, 60, and 80 and found that the emission will always be dominant by three super-radiant states. Protsenko et al.[21] studied the super-radiance of several hundred atoms (emitters) near a metal nanoparticle in a hope to develop a plasmonic nano laser, they found collective states of emitters.

For both Raman scattering and fluorescence, their enhancement factors can be modeled using one universal equation.[19-21,26] As will be discussed in the computational model and method section, both of the phenomena are closely related to the change of the radiative decay rate (RDR) of the molecules with and without the presence of metal nanostructures. For the simplicity of discussion, we only calculated and discussed the change of the RDR of the molecule at the emission wavelength. In the study, we found that the RDR enhancement factor at the emission wavelength will be drastically changed when two or more emitters arranged near one metal surface are radiating simultaneously in comparison to that of one emitter. For a spherical silver particle with a radius of 10 nm, at the resonance wavelength of 400 nm, the highest enhancement factor of RDR can be as high as 250 and the lowest enhancement factor is

also above 50 when only one emitter is considered. However, the enhancement factor at the wavelength of 400 nm is reduced to less than 2.5 when three emitters are placed near the metal surface along the positive direction of X, Y, and Z axes. The enhancement factor is reduced by a fold of 100 (or 20) in comparison to the highest (or lowest) enhancement factor of 250 (or 50) when only one emitter is included. When six emitters are evenly placed near the metal surface along three perpendicular directions, the enhancement factors drop further and exhibit an asymmetric resonance line shape near the resonance wavelength of the metal nanoparticle. The distance dependence studies show that the coupling between the metal nanoparticle and one emitter placed along the dipole axis direction is attributed to near field effect. However, the coupling among the metal nanoparticle and six or more emitters follows a far field coupling pattern.

METHODS

To calculate the enhancement factors of the RDR of multiple emitters near a metal nanoparticle, we used the software and models developed in the Zou lab based on the T-matrix method.[27-30] In this section, we explain and clarify how the enhancement factors of both Raman scattering and fluorescence are related to the calculated enhancement factors of the RDR of emitters.

For emitters with radiative and non-radiative decay rate constants k_r and k_{nr}, their quantum yield η can be expressed by the following equation.

$$\eta = \frac{k_r}{k_r + k_{nr}}. \quad (1)$$

When emitters are placed near a metal nanoparticle, the energy transfer between the emitters and the metal nanoparticle as well as their coupling will alter the radiative and non-radiative

decay rate of the system. The modified quantum yield η' of the system including both the emitters and the metal nanoparticle can be expressed by

$$\eta' = \frac{k_r'}{k_t + k_{nr}} = \frac{f_r \times k_r}{f_t \times k_r + k_{nr}} \quad (2)$$

where k_r' is the radiative rate constant of the total system, $k_t = k_{NET} + k_r'$, and k_{NET} represents the non-radiative energy transfer between the emitters and the metal nanoparticle, $f_r = k_r'/k_r$ is the enhancement factor of the RDR of the system with and without the metal nanoparticle, and $f_t = k_t/k_r$.

For the enhancement factors of both Raman scattering and fluorescence, they can be calculated using one unified equation[19]

$$f = |E/E_0|_{\lambda_1}^2 \frac{\eta'}{\eta} = |E/E_0|_{\lambda_1}^2 \frac{f_r}{f_t \times \eta + 1 - \eta} \quad (3)$$

where $|E/E_0|_{\lambda_1}^2$ is the enhanced local electric field at the excitation wavelength λ_1. For the Raman scattering, the quantum yield is very small, and Equation 3 can be simplified to

$$f = |E/E_0|_{\lambda_1}^2 f_r \quad (4)$$

For the spherical nanoparticle, f_r has been proved to be proportional to the enhanced local electric field when only one emitter is considered.[3] To avoid the complication of discussion due to different quantum yields of emitter, all the calculated enhancement factors refer to f_r which is the enhancement factor of the RDR of the system with and without the metal nanoparticle at the emission wavelength. Please note that we only calculated the enhancement factor of RDR, the reported values cannot be directly applied to the enhanced/quenched fluorescence. Equation 3 or 4 should be used to calculate the enhanced/quenched fluorescence or enhanced Raman scattering.

RESULTS AND DISCUSSION

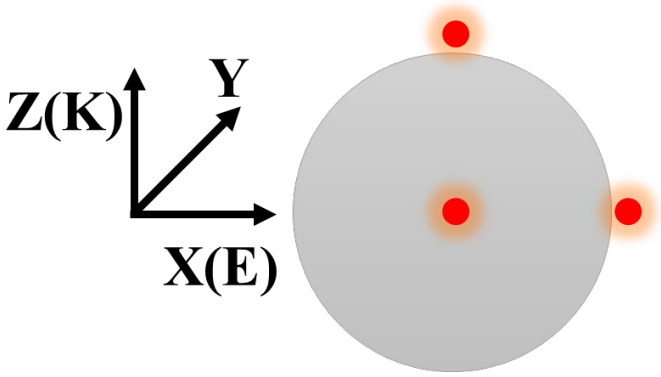

Figure 1 Schematic of three emitters radiating simultaneously near a spherical metal nanoparticle. K: Wave vector, E: Electric field.

In all the following calculations and discussion, the enhancement factors refer to the enhancement/quenching factors of the RDR of emitters at the emission wavelength with and without the presence of the metal nanoparticle. Figure 1 shows the schematic of three emitters radiating simultaneously near a spherical metal nanoparticle. In all the simulations, a spherical Ag particle with a radius of 10 nm is used. The emitters are excited by a laser beam propagating along the Z axis with a polarization direction parallel to the X axis. The polarization of the excited dipole of the emitter is along the X axis. In the initial attempt, we assume that the phase of the emitted photon is determined by their relative positions along the Z axis which is not exactly accurate and will be revised in the future study. The dielectric constants of the silver were obtained from Palik's book.[31] The medium is taken as water.

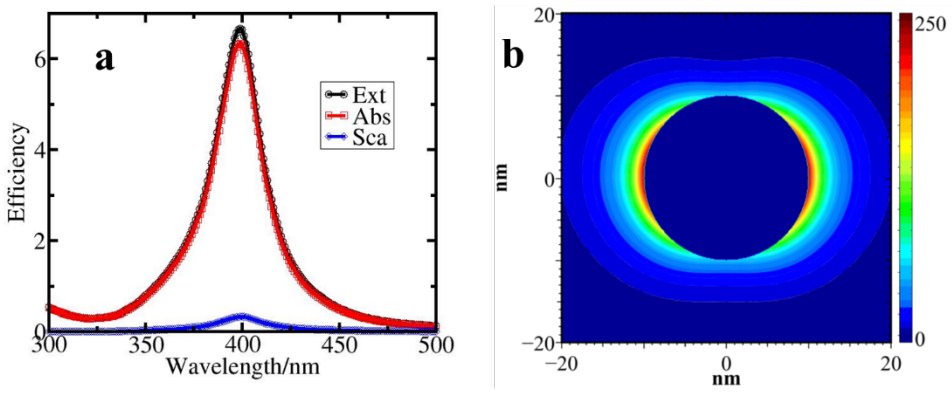

Figure 2 (a) Extinction, absorption, and scattering spectra for the Ag spherical particle with a 10 nm radius in water. (b) Enhanced electric field $|E/E_0|^2$ contour plot of the Ag sphere in the XZ plane at the wavelength of 400 nm.

The extinction, absorption, and scattering spectra of the 10 nm radius silver sphere in water are shown in Figure 2a. The resonance wavelength of the sphere is at around 400 nm. The enhanced electric field, $|E/E_0|^2$, contour plot of the sphere at the wavelength of 400 nm in the XZ plane is shown in Figure 2b. The highest enhanced local electric field over 250 can be obtained along the polarization (X axis) direction. The lowest enhanced local electric field along the Z axis is also above 50. The value of the lowest enhanced local electric field, 50, at the resonance wavelength of 400 nm is especially important for the following discussion. According to the previous theory when one emitter is considered,[3] the value indicates that the enhancement factor of RDR can only be larger than 50 no matter where the emitter is placed. However, in Figure 3, we will show that the enhancement factor can be much less than 50 when three or more emitters are radiating simultaneously near the metal surface.

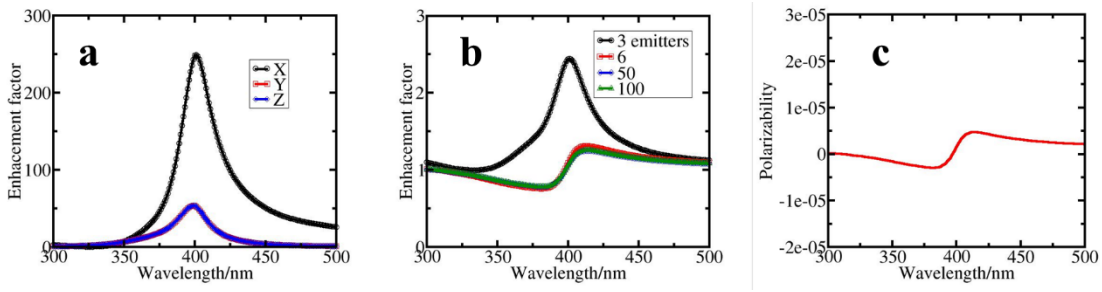

Figure 3 Enhancement factors of RDR at different wavelengths when (a) one and (b) multiple emitters are placed near the metal surface. (c) real part of the polarizability of the silver sphere (unit: μm^3).

We start from calculating the enhancement factor of RDR when one emitter is placed near the metal surface. For calculations in Figures 3-5, the emitters are placed 0.2 nm distance away from the particle surface and the value is arbitrarily chosen. The effect of particle distance on the enhancement factor is shown in Figure 6. The enhancement factor of RDR is calculated by dividing the emission cross section of the system including both N emitters and metal nanoparticle by the emission cross section from N emitters only, where N represents the number of emitters. The number of emitters is varied from one to 100. Figure 3a shows the enhancement factor of RDR when one emitter is placed along the X, Y, or Z axis near the particle surface. The highest enhancement factor of about 250 at the resonance wavelength of 400 nm is obtained when the emitter is placed along the X axis which is consistent with the electric field contour plot shown in Figure 2b. When the emitter is placed along the Y or Z axis, the enhancement factor is much weaker; however, the enhancement factor is still larger than 50 at the resonance wavelength of 400 nm which is also consistent with the enhanced local electric field near the metal surface.

Figure 3b shows the enhancement factors of RDR at different wavelengths when 3, 6, 50, or 100 emitters are simultaneously radiating near the metal surface. Three emitters are placed along the positive direction of the X, Y, and Z axes. For the 6, 50, and 100 emitters, they are arranged evenly around the nanoparticle. When there are six emitters, each two of them are arranged along the positive and negative directions of the X, Y, or Z axis. For the cases of 50 and 100 emitters, we obtained their coordinates by assuming there are 50 or 100 positive charges on a spherical surface and minimizing the energy of the system by Monte Carlo method. Figure 3b indicates that the highest enhancement factor of RDR is obtained at the resonance wavelength of 400 nm when three emitters are included. However, the highest enhancement factor is only less than 2.5 which is 100 time smaller in comparison to the enhancement factor of about 250 when one emitter is placed along the X axis. The enhancement factor is also 20 folds less when comparing with the lowest enhancement factor of 50 at the wavelength of 400 nm when one emitter is placed along the Y or Z axis.

When six emitters are evenly arranged near the particle surface along the X, Y, and Z axes, the enhancement factor of RDR at different wavelengths exhibits an asymmetric line shape near the resonance wavelength of 400 nm. When 50 or 100 emitters arranged evenly near the particle surface radiate simultaneously, there is only a slight change to the enhancement factor and the asymmetric line shape. We also carried out calculations when more than 100 emitters are included, the calculations are converged and there is no further noticeable change to the asymmetric line shape. We believe that the convergence of the asymmetric line shape is due to the convergence of the local electric field over the number of emitters at the central particle coordinate from all emitters when the number of emitters is over six.

Quite interestingly, when we calculate the polarizability of the silver nanoparticle,[32] the real part of the polarizability in Figure 3c shows a very similar asymmetric line shape as that in Figure 3b. Figure 3c indicates that the enhancement factor of multiple emitters near a metal nanoparticle is associated with the polarizability of the central nanoparticle. This is understandable since the enhancement factor of RDR is determined by the interaction between the central particle and the emitters and the induced dipole of the central particle is proportional to its polarizability. It is still a mystery for us on why the real part of the polarizability is important and we keep working on figuring out logics behind the calculation results.

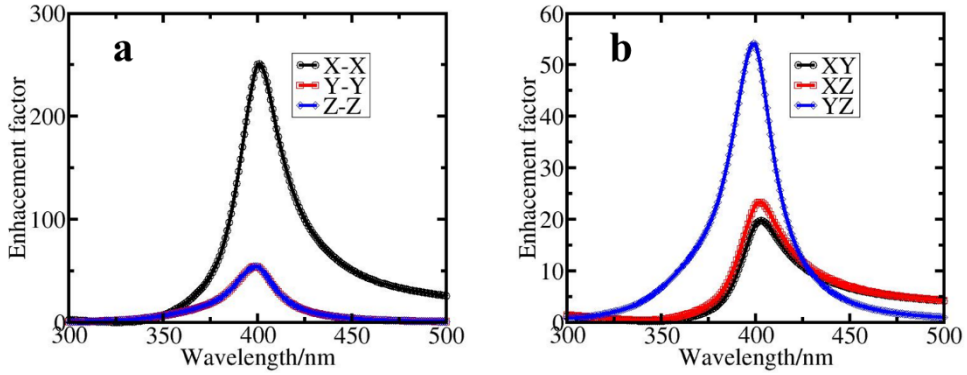

Figure 4 Enhancement factors of RDR at different wavelengths when two emitters are placed near a silver sphere. (a) The two emitters are placed at two ends of the axis along the X, Y, or Z axis. (b) The two emitters are placed perpendicular to each other along two different axes.

To further reveal more physical insights associated with the mechanism leading to the asymmetric line shape observed in Figure 3b, we calculated the enhancement factor of RDR when only two emitters are simultaneously radiating near the metal nanoparticle. Figure 4a shows the enhancement factors at different wavelengths when the two emitters labelled as X-X,

Y-Y, or Z-Z are placed at both the positive and negative sides along either X, Y, or Z axis. When the two emitters are placed symmetrically at two sides of one axis, the enhancement factors are very similar to those of one emitter arranged along the corresponding axis as shown in Figure 3a. When the two emitters are placed at two perpendicular axes either along XY, YZ, or XZ axes, Figure 4b shows that the enhancement factors of RDR of the emitters placed along YZ axes are very similar to those placed along the Y-Y or Z-Z axis as shown in Figure 4a. However, the enhancement factors drop significantly at the resonance wavelength of 400 nm when the two emitters are placed along the XY, or XZ axes. The enhancement factors at the wavelength of 400 nm are reduced to below 25. The enhancement factors at shorter wavelengths are reduced more significantly; however, those at longer wavelengths are even lifted. The profile of the spectrum evolves toward an asymmetric line shape.

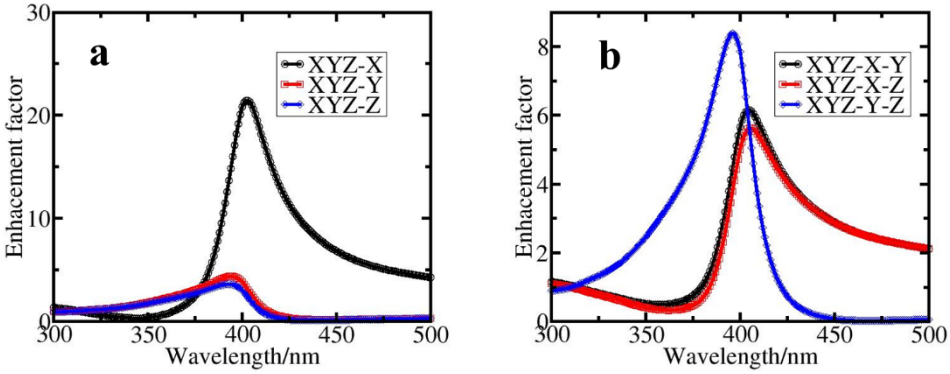

Figure 5 Enhancement factors of RDR at different wavelengths when (a) four or (b) five emitters are placed near a silver sphere.

When four or five emitters are placed near the metal nanoparticle, the coupling between emitters and the central particle which leads to the asymmetric line shape becomes more obvious. Figure 5a displays the enhancement factors of RDR of four emitters arranged near the metal nanoparticle. XYZ-X indicates that three emitters are arranged along the positive direction

along the X, Y, and Z axes, and one emitter is placed along the negative direction of the X axis. Quite interestingly, when four emitters are arranged with the pattern of XYZ-X, the enhancement factors are very similar to those of two emitters which are arranged along XY or XZ axes as shown in Figure 4b. They are all much weaker in comparison to those when the two emitters are arranged along the X-X direction as shown in Figure 4a, however they are stronger than those of three emitters as shown in Figure 3b. When four emitters are arranged with the pattern of XYZ-Y or XYZ-Z, the profiles of the enhancement factor at different wavelength are very similar, whilst the asymmetric pattern of the line shape becomes reversal in comparison to the case when they are arranged with the pattern of XYZ-X.

Figure 5b shows the enhancement factors of RDR at different wavelengths when five emitters are placed near the metal nanoparticle. XYZ-X-Y represents the arrangement when three of the five particles are placed along the positive direction of the X, Y, and Z axes while the other two of them are arranged along the negative direction of the X and Y axes. The enhancement factors are reduced further, and the highest enhancement factor is only less than nine when the five emitters are arranged in the pattern of XYZ-Y-Z. The profile of the spectrum for emitters arranged at this pattern looks like those of four emitters arranged at the pattern of XYZ-Y and XYZ-Z. When five emitters are arranged with the patterns of XYZ-X-Y or XYZ-X-Z, the profiles of the enhancement factor at different wavelengths appears to be similar to those of 6, 50, or 100 emitters as shown in Figure 3b.

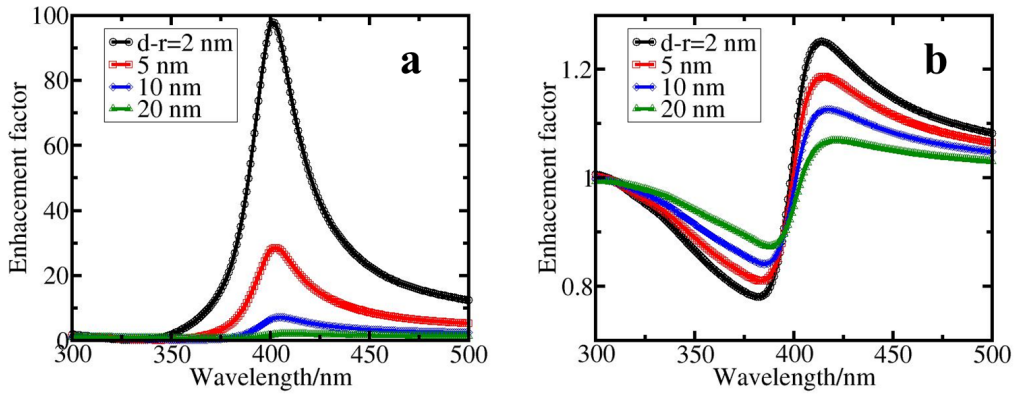

Figure 6 Enhancement factors of RDR for (a) one or (b) six emitters placed at different distances from the particle surface.

For simulations shown in Figures 3-5, we placed the emitters very close to the metal nanoparticle surface with a distance, *d*-*r*, of 0.2 nm where *r* is the radius of the metal nanoparticle. We have mentioned in the previous paragraph that we only calculated the enhancement factor of the RDR, fr, of the molecule in equations 2-4 for the simplicity of discussion, the quenching effect of the metal nanoparticle on the emission as shown in Equation 3 is not considered in all the calculations. If the quenching effect was included, the calculated enhancement factor of emission, f, will be much smaller than the reported values when emitters are placed 0.2 nm away from the particle surface. It is well known that the distance between emitters and the nanoparticle surface has significant effects on their coupling strength. For an oscillating dipole, its electric field along the dipole axis drops with increasing distance, *d*, from the dipole center. The intensity is proportional to d^{-3} and is called near field effect. When the distance is further increased, the intensity of the electric field along the direction perpendicular to the dipole axis becomes more important and the intensity decreases with a rate proportional to d^{-1}. Figure 6 shows the distance dependence of emitters from the metal nanoparticle surface when one or six emitters are placed at different distances from the particle surface. When on emitter is

placed near the metal nanoparticle surface along the X axis, Figure 6a shows that the enhancement factor at the wavelength of 400 nm drops from 97 to 6.5 when the distance between emitters and the metal nanoparticle surface, *d*-*r*, is changed from 2 nm to 20 nm. If we fit the curve of enhancement factor versus the distance between the emitter and the metal nanoparticle center, *d*, the fitting shows a power of -5.7 dependence indicating the near field effect of the enhancement. When six emitters are arranged evenly near the metal nanoparticle surface along three axes directions, Figure 6b shows that the enhancement factor gradually approaches to one. However, the distance dependence is not as dramatic as that for one emitter. If we take the wavelength at 415 nm, the enhancement factor drops from 1.25 to 1.06 when the distance, *d*-*r*, is changed from 2 to 20 nm. The least square fitting shows that the enhancement factor of RDR is proportional to $d^{-1.2}$ indicating that the coupling follows a far field pattern. The calculation results show that the enhancement factor of one emitter placed along the dipole axis direction is determined by the near field effect whilst the enhancement factor of six emitters shows more far field characteristic.

CONCLUSIONS

In conclusion, we investigated the enhancement factors of the RDR when multiple emitters radiate simultaneously near a silver nanoparticle of 10 nm in radius. The calculation results show that the enhancement factor is gradually reduced with increasing number of emitters near the metal nanoparticle. The enhancement factor of the RDR of three emitters arranged near the metal nanoparticle surface drops over 100-fold in comparison to the highest enhancement factor of one emitter at the resonance wavelength. There are also exceptions, for example, the enhancement factors for four or five emitters can be larger than those of three emitters. The profile of the

enhancement factor at different wavelength exhibits an asymmetric line shape near the resonance wavelength of the nanoparticle at 400 nm when more than six emitters are included. The profile of the asymmetric line shape is converged with increasing number of emitters and is similar to that of the real part of the polarizability of the central nanoparticle. When one emitter is placed along the dipole axis direction at different distances from the metal nanoparticle surface, the coupling between the emitter and the metal nanoparticle exhibit to be a near field effect. For more than six emitters arranged evenly around the metal nanoparticle surface at different distances, the coupling among emitters and the metal nanoparticle show a far field coupling pattern. The discoveries will advance our fundamental understanding of the enhancement and quenching mechanism of emitters near metal nanoparticle surfaces.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

RDR, radiative decay rate.

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