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Two-photon-excited Fluorescence Enhancement Caused by Surface Plasmon Enhanced Exciting Light

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Abstract: Two-photon-excited fluorescence (TPEF) enhancement effect in CdSe quantum dot modified Au nanoparticle was theoretically investigated. TPEF enhancement factor was obtained in dipole approximation by taking surface plasmon resonance enhancement effect and nonradiative energy transfer to Au NP into account. An available method to achieve sufficient TPEF enhancement factor with noble metal nanoparticles was concluded from the analysis of numerical simulation. Greater TPEF enhancement effect will be obtained by adjusting the surface plasmon resonant peak of noble metal nanoparticles to the excitation wavelength. This theoretical analysis result was proved to be appropriate to the reported experimental results.

Key words: noble metal nanoparticles; surface plasmon; two-photon-excited fluorescence; energy transfer
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激发光的表面等离激元增强效应导致的双光子荧光增强

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摘要: 理论上研究了吸附在金纳米颗粒表面的CdSe量子点的双光子荧光增强效应。在偶极近似下,全面地考虑了金纳米颗粒的存在造成的表面等离激元共振增强效应和以金纳米颗粒作为受体的非辐射能量转移效应,给出了金纳米颗粒对量子点双光子荧光的增强因子。通过数值模拟,给出了将贵金属纳米颗粒更有效地用于增强双光子荧光的方法,即将贵金属纳米颗粒的表面等离激元共振峰调至激发波长处,尽可能地增大激发光的表面等离激元共振增强效应。上述理论分析结果很好地验证了已经报道的实验结果。

关 键 词: 贵金属纳米颗粒; 表面等离激元; 双光子荧光; 能量转移

1 Introduction

Two-photon-excited fluorescence (TPEF) is a third order nonlinear optical process, the excitation probability scales quadratically with the incident light, confining it to the proximate vicinity of the

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focal plane of a focused beam. Therefore the spatial resolution is observably increased[1], which induced widely applications of TPEF in confocal imaging[2-4]. Composite systems consisted of metal nanoparticles (NPs) represent opportunities to enhance optical responses, such as surface-enhanced Raman scattering[5], second harmonic generation[6], surface-enhanced fluorescence[7]. More recently, metal NPs have been applied to TPEF. The mechanism of metal NPs enhanced TPEF was supposed to be the surface plasmon resonance(SPR) enhancement of local optical field[8-10], near-field scattering effect[11] and the absorption cross section of TPEF[12-13]. However, nonradiative energy transfer from fluorophore to metal NPs occurs on the appropriate condition[14-15], which results in the fluorescence quenching. A more effective method to use noble metal NPs to enhance TPEF would be obtained when the enhancement and quenching effects are both taken into account.

A theoretical investigation of TPEF enhancement in a composite system combined with Au NPs and semiconductor quantum dots (SQDs) was taken in this paper. SPR enhancement of the exciting light and radiative rate of the SQD, and nonradiative energy transfer from SQD to Au NP were taken into account. An available result was obtained which can be used as a guideline for metal NPs-enhanced TPEF. This result was verified by a published experiment data[16].

2　Formalism

TPEF intensity should be generally expressed by the following expression when $I_0\beta D \ll 1$[17]:

$$I_{\text{fluo}} \propto \Phi I_0^2 \beta D, \tag{1}$$

Where $\Phi = \gamma_{\text{rad}}/(\gamma_{\text{rad}} + \gamma_{\text{nonrad}})$ is quantum yield of the fluorophore and I_0, β, D are the incident light intensity, two photon absorption coefficient and the thickness of the sample, respectively. It is known that the incident light and the radiative rate of fluorophore can be modified strongly in the presence of metal NPs:

$$\begin{aligned} I &= P(\lambda_0) I_0, \\ \gamma_{\text{rad}} &= P(\lambda)\gamma_{\text{rad}}^0, \end{aligned} \tag{2}$$

Where I_0 and γ_{rad}^0 are the incident intensity and radiative rate of the fluorophore in the absence of the metal NPs, λ and λ_0 are emission and incident laser wavelength. $P(\lambda)$ is the electromagnetic-field enhancement factor, which can be obtained by solving Laplace equation describing the potential distribution around a conductor sphere in uniform electric field.

$$P(\lambda) = \left| 1 + 2\frac{\varepsilon_{\text{m}}(\lambda)-\varepsilon_0}{\varepsilon_{\text{m}}(\lambda)+2\varepsilon_0}\left(\frac{R_0}{R}\right)^3 \right|^2, \tag{3}$$

Where ε_{m} and ε_0 are the dielectric constants of metal NPs and medium respectively. R_0 and R are the radius of metal NPs and the distance to the center of sphere. We use the following formula to describe the nonradiative energy transfer rate at emission wavelength λ[15]:

$$\frac{\gamma_{\text{et}}(\lambda)}{\gamma_{\text{rad}}{}^0(\lambda)} = \frac{6}{R^6}R_0^3\left(\frac{\lambda}{2\pi}\right)^3 \cdot \frac{1}{\varepsilon_0^{2.5}}\text{Im}\left[\frac{\varepsilon_{\text{m}}(\lambda)-\varepsilon_0}{\varepsilon_{\text{m}}(\lambda)+2\varepsilon_0}\right]. \tag{4}$$

Eq. (4) depicts the non radiative energy transfer effect in dipole approximation when the surface distance between metal NPs and SQD is far. In this condition TPEF intensity should be expressed by the following expression:

$$I_{\text{fluo}}{}^*(\lambda) \propto \frac{P(\lambda)\gamma_{rad}{}^0 P^2(\lambda_0) I_0{}^2(\lambda_0)\beta D}{\gamma_{\text{nonrad}} + P(\lambda)\gamma_{\text{rad}}{}^0 + \gamma_{\text{et}}}, \tag{5}$$

The enhancement factor of TPEF is

$$A(\lambda) = P^2(\lambda_0)\frac{P(\lambda)}{P(\lambda) + \gamma_{\text{et}}/\gamma_{\text{rad}}{}^0}, \tag{6}$$

When the quantum yield of the SQD $\Phi \approx 1$, $P^2(\lambda_0)$ is the TPEF enhancement factor when SPR effect is considered only. The electromagnetic-field enhancement factor $P(\lambda)$ (Eq. (3)) and nonradiative energy transfer rate $\gamma_{\text{et}}(\lambda)/\gamma_{\text{rad}}{}^0(\lambda)$ (Eq. (4)) are the function of the dielectric constants of surrounding medium ε_0. The resonant peak of $P(\lambda)$ and $\gamma_{\text{et}}(\lambda)/\gamma_{\text{rad}}^0(\lambda)$ can be adjusted by changing ε_0.

3　Results and Discussion

The application condition of Eq. (4) in reference [15] is dipole approximation which is fixed in the condition that the surface distance is appropriate. In reference [15], the parameters of the composite system were: $R_{\text{Au}} = 6.5$ nm, $R_{\text{CdSe}} = 3.75$ nm, $\Delta = 9$ nm, Δ is surface distance between Au NPs and CdSe SQD. The TPEF enhancement of this

composite system was calculated. The wavelength of the exiting light was supposed to 780 nm. The dielectric constants of Au NPs we used were given by Johnson and Christy in 1972[18]. Forty dielectric constants of Au in forty incident light wavelength from 400 nm to 800 nm were obtained by interpolating to the polynomial fit of the dielectric constants given by Johnson and Christy.

Fig. 1 represents the curves of $P(\lambda)$, $\gamma_{et}(\lambda)/\gamma^0_{rad}(\lambda)$ and TPEF enhancement factor $A(\lambda)$ with and without the nonradiative energy transfer considered. The dielectric constants of surrounding medium $\varepsilon_0 = 2.2$. The resonant peaks of $P(\lambda)$ and $\gamma_{et}(\lambda)/\gamma^0_{rad}(\lambda)$ are near 550 nm. Since the existence of nonradiative energy transfer, the TPEF enhancement factor was reduced compared to that without the nonradiative energy transfer taken into account. In the resonant region of nonradiative energy transfer, $A(\lambda) < 1$, the TPEF intensity is quenched.

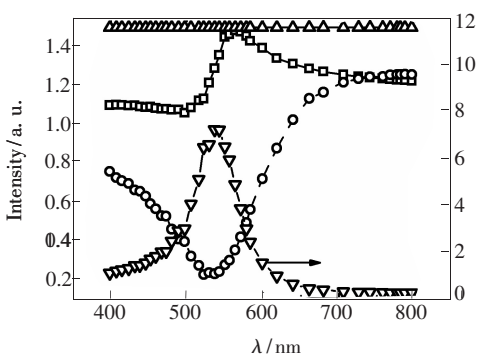

Fig. 1 The electromagnetic-field enhancement factor $P(\lambda)$ (□), nonradiative energy transfer rate $\gamma_{et}(\lambda)/\gamma^0_{rad}(\lambda)$ (▽), and the TPEF enhancement factor $A(\lambda)$ with(○)and without (△) nonradiative energy transfer effect taking into account. The dielectric constants of surrounding medium $\varepsilon_0 = 2.2$.

ε_0 was set to 10.9 to adjust the resonant peak of $P(\lambda)$ and $\gamma_{et}(\lambda)/\gamma^0_{rad}(\lambda)$ to the exiting wavelength 780 nm. Fig. 2 represents the calculated results. The enhancement of the exiting light is increased, and the nonradiative energy transfer rate of the emission region (wavelength is shorter than 780 nm) is reduced. Thus the TPEF enhancement factor is obviously increased. In the emission region far from the exiting light, 400~600 nm region in Fig. 2,

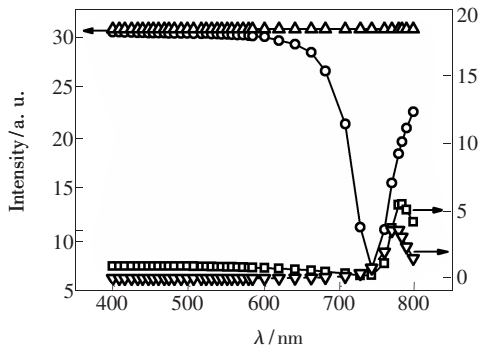

Fig. 2 The electromagnetic-field enhancement factor $P(\lambda)$ (□), nonradiative energy transfer rate $\gamma_{et}(\lambda)/\gamma^0_{rad}(\lambda)$ (▽), and the TPEF enhancement factor $A(\lambda)$ with(○)and without (△) nonradiative energy transfer effect taking into account. The dielectric constants of surrounding medium $\varepsilon_0 = 10.9$.

the TPEF enhancement factors with and without nonradiative energy transfer taken into account have almost the same values, which indicates that the nonradiative energy transfer effect can be neglected in this condition.

The position and intensity of SPR peak of Au NPs could be adjusted by changing the dielectric constants of the surrounding medium, as shown in Fig. 3. The enhancement of exiting light (780 nm) is drastically increased by adjusting the SPR peak to the exiting region. Fig. 4 represents the TPEF enhancement factor in the condition of Fig. 3. As the SPR peak was adjusted to the exiting region by increasing ε_0, the TPEF enhancement factor of emission region is enlarged tremendously. An effective method to enhance TPEF by noble metal NPs is

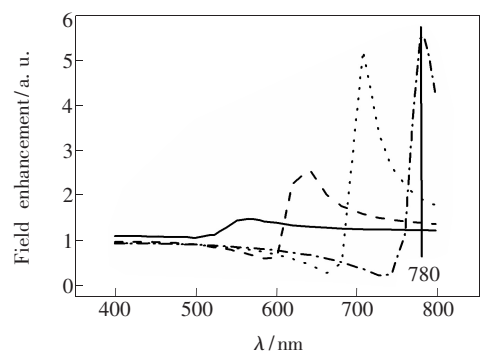

Fig. 3 The field enhancement factor $P(\lambda)$ of Au NP when the dielectric constants of the surrounding medium is 2.2 (solid), 5.2 (dash), 8.2 (dot) and 10.9 (dash dot).

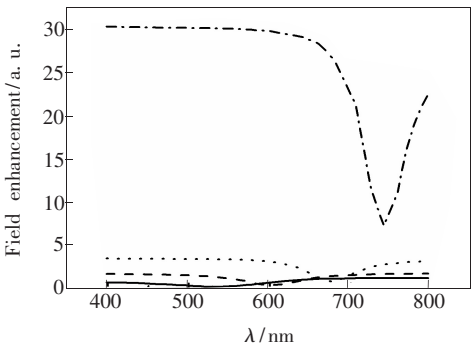

Fig. 4　TPEF enhancement factor $A(\lambda)$ when the dielectric constants of the surrounding medium is 2.2 (solid), 5.2 (dash), 8.2 (dot) and 10.9 (dash dot).

concluded, which is that greater TPEF enhancement factor will be obtained by adjusting the SPR peak of noble metal NPs to the exiting light region through changing size, shape and medium dielectric constant of metal NPs.

In reference [16], J. Lukomska *et al*. published their experimental results of two-photon induced fluorescence enhancement on silver colloids. The experimental results manifested that large SPR intensity of silver colloids in the exiting light region resulted in a large TPEF enhancement. The experimental results certificate the theoretical results in this paper.

4　Conclusion

In summary, TPEF enhancement of a composite system combined with an Au NPs and SQD was investigated theoretically. SPR enhancement of the exciting light and radiative rate of the SQD, and nonradiative energy transfer from SQD to Au NP were taken into account. Nonradiative energy transfer effect will reduce the TPEF enhancement factor. When the SPR peak is adjusted to the exiting light region, nonradiative energy transfer effect in the emission region can be neglected, and a greater TPEF enhancement factor will be achieved. Thus it is a better method to get a large TPEF enhancement factor by adjusting the SPR peak of noble metal NPs to the exiting light region.

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