Recent Progress on Plasmon-Enhanced Fluorescence

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Abstract: The optically generated collective electron density waves on metal–dielectric boundaries known as surface plasmons have been of great scientific interest since their discovery. Being electromagnetic waves on gold or silver nanoparticle’s surface, localised surface plasmons (LSP) can strongly enhance the electromagnetic field. These strong electromagnetic fields near the metal surfaces have been used in various applications like surface enhanced spectroscopy (SES), plasmonic lithography, plasmonic trapping of particles, and plasmonic catalysis. Resonant coupling of LSPs to fluorophore can strongly enhance the emission intensity, the angular distribution, and the polarisation of the emitted radiation and even the speed of radiative decay, which is so-called plasmon enhanced fluorescence (PEF). As a result, more and more reports on surface-enhanced fluorescence have appeared, such as SPASER-s, plasmon assisted lasing, single molecule fluorescence measurements, surface plasmon-coupled emission (SPCE) in biological sensing, optical orbit designs etc. In this review, we focus on recent advanced reports on plasmon-enhanced fluorescence (PEF). First, the mechanism of PEF and early results of enhanced fluorescence observed by metal nanostructure will be introduced. Then, the enhanced substrates, including periodical and nonperiodical nanostructure, will be discussed and the most important factor of the spacer between molecule and surface and wavelength dependence on PEF is demonstrated. Finally, the recent progress of tip-enhanced fluorescence and PEF from the rare-earth doped up-conversion (UC) and down-conversion (DC) nanoparticles (NPs) are also commented upon. This review provides an introduction to fundamentals of PEF, illustrates the current progress in the design of metallic nanostructures for efficient fluorescence signal amplification that utilises propagating and localised surface plasmons.

Keywords: Enhanced fluorescence; metallic nanostructure; Surface plasmon plarion

1 Introduction

Since Prof. Ritchie firstly predicted that the existence of self-sustained collective oscillations at surface of metallic nanostructure by consideration of energy losses characteristic of fast electrons transmitting across optically thick metallic films in 1957 [1], the collective electron density waves on metal surface known as surface plasmons (SPs) have been of great scientific interest in theoretical and experimental studies [2–9]. Largely enhancement of the local electromagnetic (EM) field induced by surface plasmon resonance (SPR), which plays an important role in studying SES, including PEF and surface-enhanced Raman scattering (SERS), have the focus of discussions [10–13]. It is
found that the characteristic of SPR (position and intensity) are critically dependent upon the geometrical parameter of the nanostructures, such as the size, shape, as well as the the composition of the nanostructure, and the dielectric constant of the surrounding environment [15–18].

With the help of excitation of SPs, the electron–photon interaction and molecular photonic state can be modulated. As a result, by using plasmonic metallic nanostructures, the variety of responsive variables give us a potential solution to study the new phenomenon appearing in many fields. Therefore, the study on the coupling effect among plasmonic metallic nanostructure substrate and surface enhanced fluorescence have been one of most active and important topics, particularly since the first classical observation of the effect of environment on the emission characteristic of a fluorophore-excited electronic state by Drexhage [19]. Although the enhanced effect is a systematic contribution from physical and chemical aspects, now it is widely recognised that the localised EM field generated at the metal surface plays a key role in the PEF effect. The SP distribution and the fluorescence emission from the fluorophores located closer to the metallic substrate can be modified by controlling the dielectric properties and shape of the metallic nanostructure. As a result, manipulation of optical nanostructure substrate with plasmonic properties is considered as the mostly promising direction in PEF research.

Particularly, better understanding of coupling and interconversion mechanism among free electrons, surface plasmon, photons, and fluorophores based on metal substrate with various shape configurations in PEF effect still should be highlighted [10, 11, 20]. In this review, we focus on the recent advancement of the effect of plasmonic nanostructures towards PEF. First, we introduce the concepts and principles of PEF. Then we discuss PEF for fluorophores coupled with SPP excited on periodical metallic nanostructure substrate, to PEF for fluorophores coupled to localised enhancement of the EM field existing on non-periodical metallic nanostructure substrate, and to PEF for the distance and wavelength dependence factor. And then, it will be demonstrated that tip-enhanced fluorescence spectroscopy (TEFS) can even be used with subdiffraction limit spatial resolution. Finally, the recent progress on PEF from the rare-earth doped UC and DC nanoparticles are also demonstrated.

2 The principle of PEF

Fluorescence, as well as photoluminescence (PL), is the property of some luminescent center, such organic molecules and rare-earth ions, to absorb photons with high energy and to emit them with low energy subsequently. The processes that occur between the absorption and the emission of photon could be demonstrated by a Jablonski diagram, which illustrates the electronic transition processes of fluorophore occurring in the excited states [22]. It is widely accepted that the excited electron transition from the upper energy level to ground level happens by two methods; one is by emitting photon, and the other is by relaxation of energy into the phonon [22]. With the condition of weak excitation, that is, far from saturation of the excited state, the fluorescence spontaneous emission rate \( \gamma^0_{em} \) can be regarded as the excitation from ground state to excited state and the subsequent relaxation back to the ground state via fluorescence emission [10, 22], i.e

\[
\gamma^0_{em} = \gamma^0_{exc} Q^0
\]

where \( Q^0 \) and \( \gamma^0_{exc} \) is the quantum yield and the excitation rate, respectively, and the superscript ‘0’ specifies that the molecule is in free space and does not couple to the local environment. The subscript ‘i’ indicates that the quantum yield is defined by the intrinsic properties of the molecule.

As indicated before, \( Q^0 \) is the probability of a photon relaxing from excited to ground state by emitting a fluorescence photon. Here, the radiative and nonradiative decay rate can be defined as \( \gamma_{em} \) and \( \gamma_{nr} \), respectively, so the intrinsic quantum yield with more general definition for \( Q^I_0 \) could be defined as below:

\[
Q^I_0 = \frac{\gamma_{em}}{\gamma_{em} + \gamma_{nr}}\frac{\gamma_{em}}{\gamma_{em} + \gamma_{nr}}
\]

If the local environment of the fluorophore has changed, the excitation and decay rates will be changed correspondingly. Then Eqs. (1) and (2) can modified as

\[
\gamma_{em} = \gamma_{exc} Q
\]

and

\[
Q = \frac{\gamma_{em}}{\gamma_{em} + \gamma_{nr}} = \frac{\gamma_{em}}{\gamma + \gamma_{nr} + \gamma_{abs} + \lambda_m}
\]

Here, \( \gamma_{abs} \) accounts for dissipation to heat into the environment and \( \gamma_m \) accounts for coupling to nonradiative electromagnetic modes, such as the emitted energy is converted into heat through the interaction between the electron and the lattice. The whole decay rate \( \gamma = \gamma_{em} + \gamma_{nr} \) defines the lifetime \( \tau = 1/\gamma \) of the excited state. In general, the fluorescence emission is not only dependent on
the molecular properties but also the external parameters accounting for the local environment of the fluorophore.

For a conventional fluorescence technique measurement, pursuing the brighter and more stable signals of the fluorophore generated by the minimisation of the internal and environmentally conditioned nonradiative processes and increasing spontaneous emission rate mainly depend upon its properties [22]. Though fluorescence is known as one of the best choice optical method for the detection of biological and chemical species, a typical disadvantage of the conventional fluorescence technique is the relatively low signal-to-noise (background) ratio, which restricts its application to important areas of medical diagnostics, food control, and security, particularly realisation of the purpose of the detection of a target fluorescent molecules on a single molecule level. So exploring a proper solution to overcome the disadvantage mentioned before has attracted great attention because of their various applications in many fields.

3 PEF from various geometrical metallic plasmonic nanostructures

3.1 Interaction of fluorophores with surface plasmons

Since the pioneering work of Purcell [23], many researchers have been demonstrated that the excited atomic state lifetime is critically dependent on the inner properties of the atom and its environment both from experimental and theoretical viewpoint [13, 22]. Due to the interaction of the fluorophore with its environment, the fluorescence processes, including both the excitation and the emission processes, can be modulated by modifying its local EM field. As a result, obtaining the limit sensitivity detection of the fluorescence signal, in order to overcome the disadvantage of the conventional fluorescence technique, can be performed by controlling the local EM field around the fluorophores. With the help of the coupled effect between the plasmon resonance with the incidence wave and fluorescence emission, the total enhancement factor (EF) can be depicted through the following equations [24, 25]:

\[
\sigma_{\text{PEF}}(\lambda_L, \lambda, d_{av}) = |M_{\text{EM}}(\lambda_L, \lambda, d_{av})|^2 \times \frac{\sigma_{FL}(\lambda_L, \lambda)}{|M_d(\lambda, d_{av})|^2} \\
= \left| \frac{E_{\text{loc}}(\lambda_L, d_{av})}{E_{\text{in}}(\lambda_L)} \right|^2 \times \left| \frac{E_{\text{loc}}(\lambda, d_{av})}{E_{\text{in}}(\lambda)} \right|^2 \\
\times \left| \frac{\sigma_{FL}(\lambda_L, \lambda)}{|M_d(\lambda, d_{av})|^2} \right| \\
= \left| M_1(\lambda_L, d_{av}) \right|^2 \left| M_2(\lambda, d_{av}) \right|^2 \\
\times \left| \frac{\sigma_{FL}(\lambda_L, \lambda)}{|M_d(\lambda, d_{av})|^2} \right|^2
\]

Figure 1: Schematic of confined field of SPP and LSP modes coupled with a fluorophore excited with an external EM field.

between the ground state and higher excited states (see Figure 1). It is reported that the internal conversion process relies critically on the electronic configuration of the fluorophore through the overlap of its wavefunctions [10]. Thus, it is important to investigate the energy transfer process between the fluorophore and the metallic nanostructure, which will help us to study the contributing effect of the modified relaxation rate of fluorophore towards the radiative emission rate.

Based on the EM mechanism, the cross-section of PEF from the metal nanostructure can be defined as

\[
\sigma_{\text{PEF}}(\lambda_L, \lambda, d_{av}) = |M_{\text{EM}}(\lambda_L, \lambda, d_{av})|^2 \times \frac{\sigma_{\text{FL}}(\lambda_L, \lambda)}{|M_d(\lambda, d_{av})|^2}
\]

Here \(|M_{\text{EM}}|^2\) is total EF, while \(|M_1|^2\) and \(|M_2|^2\) are EFs related with the coupled effect between SPR with the incident wave and fluorescence emissions, respectively.
\(\sigma_{FL}(\lambda, \lambda)\) and \(\sigma_{PEF}(\lambda, \lambda)\) are the scattering cross-sections of fluorophore in the free space and local field, respectively, and \(|M_{spw}|^2\) is factor that shows the energy transfer from the fluorophore to the metal substrate.

From Equation (5), the fluorescence enhanced effect shows a balance between several processes including the increase of excitation rate by the local EM field, a radiative decay rate enhancement by SPCE, and quenched effect due to the nonradiative energy transfer from the fluorophore center to the metallic substrate, all of which critically depend on the distance between the fluorophore center and the metallic substrate [26].

From the point of view above, PEF is a multiprocess system, and the enhanced effect depends on many critical factors. In this section, we will review the recently progress of enhanced fluorescence effect from the periodical and nonperiodical type plasmonic nanostructures, such as nanograting, nanohole arrays and so on, and then the selective of excitation condition and distance-dependent effects are also discussed.

### 3.2 PEF from periodical metallic plasmonic nanostructure

Coupled with incident light, SPR acts as an efficiency interaction platform for the detection of fluorophores with high sensitivity. In general, due to the existence of a mismatch in wave vector momentum of the SPPs and the incident light, the excitation of SPPs on a flat continual metal surface is difficult to realise [27]. So it is difficult to obtain the potential plasmonic coupling as well as efficiency of the fluorescence enhancement effect on the metal substrate with flat morphology [30]. It is shown that the mismatch can be overcome by introduction of an external periodical metal surface such as gratings, nanohole arrays, nanocaps arrays, and so on.

#### 3.2.1 PEF from Nanograting substrate

The first observation of anomalies in the intensity distribution of diffraction spectrum from a metallic grating by Wood in 1902 [28], which was later interpreted based on the relationship between the incident photon and a SPR that existed in the grating surface [29]. So fabricating the metal surface with a periodic nanoscale corrugation provides an excellent candidate, that is, the momentum conservation restriction could be relaxed by breaking the translational invariance of the substrate. For the excitation of grating-coupled SPR, the excited condition can be defined as

\[
K_{sp} = K_{px} + P = \frac{2\pi}{\lambda} \sqrt{\varepsilon_m(\omega) \sin \theta + \frac{2\pi}{\lambda} m}
\]

Here \(\lambda\) is the grating period, \(\lambda\) is the incident light wavelength, \(m\) is the diffraction order, \(\theta\) is the incidence angle, and \(\varepsilon_m(\omega)\) is the frequency-dependent dielectric function of metal given by Drude model.

The mismatch in the wave vector between the in-plane momentum \(K_x = K \sin \theta\) of impinging photons can also be overcome by using diffraction effects at a grating pattern on the substrate. As a result, the moderated diffraction on periodically corrugated metallic surfaces provides an alternative method for simultaneous SPP-enhanced excitation at \(\lambda_{ab}\) and extraction of SPP-driven emission of fluorescence light at \(\lambda_{em}\). By fabricating a series of tailored silver plasmonic grating nanostructure, Tawa systematically investigated the relationship between the grating parameters (depth and duty ratio) and the fluorescence enhanced effect [30, 31], and found that at a depth of 20 nm and duty ratio equal to 0.43, the fabricated grating substrate achieves optimal fluorescence enhancement. It is found that the fluorescence enhancement mechanisms from grating arise from both the SPP-enhanced absorption and SPCE. Sun also adapted silver sinusoidal nanograting as the enhanced substrate to boost the fluorescence intensity of target molecules as high as 30-fold [32], as shown in Figure 2. With the help of photoluminescence (PL) measurements, the author found that enhanced effect is periodical and angular-dependent. That is, the SPP-enhanced absorption effect turn to weakens the larger grating pitch, while SPCE becomes the dominant factor for enhancement. And the directional emission of high p-polarisation of SPCE at different detection angles is observed experimentally [33]. With the increase of the metal film thickness in the grating-based SPCE system, the enhanced spectra was demonstrated to be significantly affected by both depth and film thickness. Furthermore, for the short wavelength range, the higher angular sensitivity is obtained [34, 35].

#### 3.2.2 PEF from nanohole array substrate

Because of the enhanced extraordinary optical transmission (EOT) effect, the substrate exhibits greater transmission of light energy than that occupied by the nanoholes [36]. The noble metal optical films decorated with subwavelength nanoholes arrays are introduced to act like an excellent antenna to couple the incident EM wave into surface plasmons at a given frequency, and both the position and the width of the transmission peak can
be modulated by adjusting the symmetry and period parameters. As a result, the position of transmission tips $\lambda_{tip}$ under normal incidence, can be given by the following dispersion relation [37]:

$$\lambda_{tip} \sqrt{i^2 + j^2} = a_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}}$$

(7)

where $a_0$ is the period pitch of hole arrays, and the $i$ and $j$ are the scattering orders of the nanohole array [38].

On a free-standing nanohole array film, the incident light coupled with the SPs can enhance the fields associated with the evanescent waves, which then increase the transmittance. As a result, continuous metallic film perforated with arrays of nanoholes can supports the excitation of SPPs and LSP [39]. The enhanced EM field will help to increase fluorescence efficiency of the fluorophore located in vicinity of substrate. In order to collect the most enhanced fluorescence signals, the peak of the LSPR should be around 40–120 meV, which is higher in energy than the emission peak of dye, and the shape of LSPR spectra should be same as the excitation spectrum of the dye [40].

The conditions of plasmon coupling, such as incidence angle, laser frequency, metal composition, and excitation and emission properties of fluorophores play an important role in PEF on the metal nanohole arrays. By using various geometric parameters of the arrays in the Au film, Brolo reported a significant enhanced fluorescence effect compared with the unpatterned identical films on glass. They found that the Au films decorated with nanohole arrays at resonance condition can improve the fluorescence sensitivity, and the detected fluorescence is strongly dependent on the nanohole radius and periodical distance, as shown in Figure 3 [41]. In order to avoid the fluorescence quenching effect, silicon oxidation film also introduced as a spacer layer to separate the fluorescent molecule from the substrate [42]. Recently, a periodical nanostructure with nanohole arrays formed in continued silver films was fabricated with template-stripping technique first and then with an atomic layer deposition grown oxide layer on
Selecting Rh6G-Quasar670™ FRET pair as the acceptor molecule, by tuning the plasmon wavelength with a maximal overlap of the acceptor excitation and donor's emission, the highest efficiency enhancement effect can be obtained by using the nanohole arrays [45]. In comparison with the back side illumination, the front side illumination stimulates a stronger coupling between the incident EM wave and the substrate [46]. Furthermore, Bai’s group systematically studied the plasmonic responses of four plasmonic metals (Au, Ag, Cu, Al) and three composite plasmonic metal (Ag/Au, Cu/Au, Al/Au) nanohole arrays in the plasmon-enhanced fluorescence spectroscopy biosensing setup [47]. In addition, a large-area golden nanohole arrays integrated with conductive glass (indium tin oxide: ITO) were also used to demonstrate the dielectrophoresis (DEP)-enhanced SPR sensing. Governed molecules diffuse to the sensor and are significantly accelerated by using applied AC electric field forces on the BSA molecules, as shown in Figure 4 [48]. It is found that the fabricated nanostructure enables label-free and real-time detection of target molecules in the concentrations as low as 1 pM in very short time. Compared with traditional diffusion-based binding method, the current protocol exhibits very highly detection efficiency.

3.2.3 PEF from nanoparticle arrays substrate

It is reported that the plasmonic properties of the nanoparticles (NP) critically depend on its characteristics, such as the dielectric constant, interparticle distance, shape, and dimension. As a result, many researches have been performed to study the fluorescence enhancement on such NP substrate, particularly the relationship between the orientation and distance of the fluorescent molecules, as well as the environment effect, with respect to the substrate [49–51]. Due to the coupling effect between the emission of the fluorophore and the SPR band of the SNP array nanostructure, the intensity of PEF influenced by adjusting the distributed characteristics of the nanoparticles arrays was also observed experimentally [52]. Though the deposition of metal nanoparticles onto the substrate often produces some local “hotspot” randomly, which will helpful to obtain a high fluorescence signal, the fluorescence-enhanced substrate with large area, and uniform and high enhanced factor is still difficult to realise [53]. With the help of the thermal deposition method, Cu periodical nanostructures were fabricated. For a longer wavelength region, LSPR of the fabricated substrate can be precisely controlled. It is found that the quenched fluorescence effects from fluorophore nearby the plasmonic pure Cu nanostructures are observed. With proper tuning of the position of SPR, the highest fluorescence enhanced factor (EF) of target molecules by 89.2-fold was obtained as compared to the reference sample, as shown in Figure 5 [54].

3.2.4 PEF from nanorod arrays substrate

The properties of LSPR critically depend on morphology of the metallic nanostructure. Compared with local enhanced EM field generated in randomly patterned metallic nanostructures, the SP near-field coupling between particle dimers can lead to the frequency shift of LSPR and unusually huge EM fields for nanostructure with order arrays. As a result, the precise tuning of LSPR, such as by adjusting the shape and arrangement of metal nanoparticles, play an important role in pursuing the high-efficiency coupling effect of the fluorophore and the local-enhanced EM field [55, 56]. It is reported that considerable fluorescence enhancement factor of 100-fold, from the silver nanorod arrays nanostructure with a regular distribution was obtained as compared to the controlled sample [57]. Recently, Abdulhalim et al. has investigated the effect of the morphology of silver nanorod arrays on the PEF with the glancing angle deposition (GLAD) method. It is found that the nanorod length plays a significant effect on the PEF enhancement factor. Based on the lighting-rod and SPR effects, the variation of PEF efficiency from silver nanorods array substrate was qualitatively analysed [58].

3.3 PEF from nonperiodical metallic plasmonic nanostructure

Spatial correlations and distribution of EM field have been extensively investigated in the study of the nature of wave transport in nonlinear disordered systems [59]. Due to the LSPs and the lightning-rod effect, which are governed by structural inhomogeneities, the correlations of local EM enhanced effect existing in disordered metallic nanostructure have been widely studied, as reviewed by V. M. Shalaev [60, 61]. The resonant dipolar excitations localised in disordered nanostructures with subwavelength size exhibiting sensitive frequency and polarisation dependence are critically determined by the local topography of the nanostructure [62]. For the giant local EM field excited in the nonperiodical structure, the spectrum properties of molecules located in the vicinity of “hotspots” that exist in the plasmonic nanostructure can be manipulated. As
films was fabricated with template-stripping technique first and then with an atomic layer deposition grown oxide layer, such as silica shell or alumina, to prevent fluorophore quenching.

Figure 3: (A) The transmission spectra of white light across nanohole arrays. The uncoated nanohole array film with pitch \( l = 440 \) nm (curve a), \( p = 550 \) nm (curve b), and coated with a dye film of oxazine 720 with \( p = 440 \) nm (curved c), B) The calculated factor of enhancement from nanohole arrays with different pitch [41].

Figure 4: A) Schematic of the experimental setup. B) Dielectrophoretic forces attract target molecules to the edge of each hole as the electric field intensity gradient is strongest (red color) along the rim of the holes. And C) The SEM image of the nanohole array (periodicity pitch \( p = 600 \) nm and nanohole diameter \( d = 140 \) nm), the scale bar here is 500 nm [48].

3.3.1 PEF from metallic silver island substrate

Fluorescence enhancement on substrates with metallic islands film was subject to research since the 1980s [63]. It offers the advantage of a relatively simple preparation method and provides moderate enhancement factors.
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Figure 5: A) SEM image acquired from the copper arrays, and B) Schematic of the interaction between the copper nanostructure and fluorophores [54].

through the combined effect of PEF excitation rate and increased quantum yield. With the help of thermal vapor deposition method, copper films with various thicknesses deposited onto glass substrate have been used to study the enhanced fluorescence effect. The experimental observations show that fluorescence intensity of fluorophores located near the Cu films critically depend on the film thickness, and reaches maximum EF at certain thicknesses [64]. It is reported that the PEF derived from coupling effect of fluorescent molecules with excited states with the SP in the metallic nanostructure and the local EM enhancement effect stimulates the enhanced absorption of the fluorophores [63, 66].

3.3.2 PEF from metallic fractal-like substrate

Due to the strong optical response fluctuations of the local EM fields, which could be moderated by adjusting the fraction dimensional and morphology of nanostructure, the nonlinear optical characteristics of disorder metal nanostructure have attracted much attention recently [61, 67, 68]. It is has been reported that fluorescence enhancement effect fluorophore emission was observed on “hotspots” located among the silver fractal nanostructure [69]. As a result, nonperodical metal nanostructures with fractals-like type have the ability to enhance a range of effects related with EM radiation effectively, such as PFE. Tanya Shtoyko observed significant fluorescence enhancement signal from the silver fractals nanostructure, when fabricated using the electrochemical reduction method. He found that the fluorescence enhancement effect is critically dependent on the topography and dielectric properties of fabricated sample [70].

Due to the LSPR, the more the “hotspots” in the fractal-like nanostructure, the stronger EF will be obtained. Zheng investigated PEF effect from the complex metallic nanostructures composed of silver fractal nanostructure and nanoparticles. Compared with silver nanoparticles (AgNPs) or pure silver fractal-like structure, the PEF EF, as high as 12-fold, was obtained from the Rh6G molecules on the fractal-like structure decorated with nanoparticles, which highlight the importance of the effect of the dimensional number in fractal nanostructure [71]. Furthermore, the simultaneous observation of SERS and PEF from target molecules, such as Rh6G, MG molecules, on Ag fractal-like structure with proper excitation condition was reported, as shown in Figure 8 [72].

The evolution of the metal nanoparticle aggregates to a thermodynamically stable flower-like dendrite nanostructure contributed to strong anisotropic growth, which can be explained with the diffusion limited aggregation (DLA) model [73]. Taking advantage of the galvanic displacement reaction method, silver flower-like dendrites nanostructures were fabricated by properly controlling the experimental conditions including the reaction time and solution concentration, and they were found to exhibit very good PEF enhancement capabilities [74]. Due to the PEF distance-dependent effect, Li studied the distance effect on the enhanced fluorescence by introducing the PAA/PDDA multilayer film as a spacer to isolate the fluorophores and silver dendrite nanostructures, while distance can be adjusted by immersion of the sample into solutions with different pH values or ionic strengths, as shown in Figure 9 [75].

3.3.3 PEF from deposited metallic nanoparticle substrate

With the help of LSPR, the local-enhanced EM fields among noble nanoparticle arrays can be formed, which indeed are helpful in moderating the emission properties of the fluorophore [76]. As a result, the investigation of the coupling effect between LSPR and the emission of the fluorophore is extremely important, while the nonradiative decay rate critically depends on the distance between the fluorophore and the metal particles. In order to prepare the PEF substrate with uniform distribution of the metal nanoparticles, the self-assembly method is often adopted in the sample fabrication process. For example, uniformed nanostructure substrate was fabricated by deposition of noble metal NPs on silanized glass substrate or employed polycarbonate (PC) films and the distribution of the nanostructure critically depends on the assembly time and solution concentration, and this substance exhibits outstanding effect for PEF [77, 78]. In order to investigate the shape-dependence on PEF effect, self-assembled nanostructures of various shapes, including nanotetrahedral, spherical,
It is reported that considerable fluorescence enhancement factor of 100-fold, from the silver nanorod arrays nanostructure with a regular distribution was obtained as compared to the controlled sample. Recently, Abdulhalim et al. has investigated the effect of the morphology of silver nanorod arrays on the PEF with the glancing angle deposition (GLAD) method. It is found that the nanorod length plays a significant effect on the PEF enhancement factor. Based on the lighting-rod and SPR effects, the variation of PEF efficiency from silver nanorods array substrate was qualitatively analyzed.

Figure 6: The SEM picture of the silver nanorods fabricated at A) room temperature (320 K) and B) low temperature (140 K), C) PEF spectra of R6G on silver nanorod array substrates with various nanorod lengths, and D) the relationship between EF and the length of nanorods.

Figure 7: The interaction between the SiF and fluorophore with the excitation external EM field.

As PEF is a property of the near-field interaction of an excited state fluorophore with the enhanced local EM field generated on the metal nanoparticle, the coupled metal NPs could produce a larger enhancement when the fluorophore is located in the proper position. It is found that the fabrication of effective PEF substrate with high local EM field or "hotspots" will produce better fluorescence enhancement. Furthermore, the simultaneous enhanced Raman and fluorescence spectrum from the gold dimer and trimer nanostructure was observed recently.
Figure 8: A) The AFM image of Ag fractal-like structure, B) the model of fractal-like structure highlighted with red line circle in a), C) the simulated EM field with 532 nm (top) and 633 nm (down), and D) the PE spectra of Rh6G molecules on reference sample(curve a), and Ag fractal-like structure (curve b) [72].

Figure 9: A) The PEF effects of Por$^{4-}$ on Ag nanostructures in different ionic strength, B) The peak PL intensity of the Por$^{4-}$ (shown in figure a) with different number PAA/PDDA bilayers [75].
Figure 10: A) The SPCE spectra of quenched/dequenched RhB molecules. Inset: the dequenched SPCE schematic. B) Angle distribution of the dequenched SPCE, C) The emission of the dequenched SPCE with polarised dependence [80].

4 The wavelength and spacer effect towards the fluorescence enhancement

Besides the morphology of the plasmonic substrate, the enhancement and quenching effect of fluorescence are also influenced by the distance between the fluorophore and the plasmonic nanostructure, and spectral characteristics [83]. By tuning the spacing between the molecules and metallic substrate, coupling effect between SPR and excited state molecules can be moderated [84]. Recently, several works have reported that the result of investigations of the distance and plasmon wavelength dependent fluorescence of fluorophore via nanorod or nanoparticle substrate [85, 86]. In particular, core–shell configuration, precisely controlling the distance between fluorophore and plasmonic nanostructure, have been widely used in the investigation of PEF effect recently [87–90]. It is found that by introduction of silica shell with various thicknesses to isolated fluorophore Au nanoparticles (AuNPs) and four different target molecules with different absorbance properties, the investigation of fluorescence quenching effect from complete quenching to no coupling was comprehensively carried out. It is found that the energy transfer from the fluorophore to the metal substrate plays a critical role in fluorescence quenching phenomenon, as shown in Figure 11 [89].

5 The tip-enhanced effect towards fluorescence emissions

Tip-enhanced Raman scattering (TERS) can resolve beyond the optical diffraction limit spatially and reveal detailed molecular information at the nanoscale [91], which is widely applied for spectrum sensing and biomolecule detection [92, 93], plasmonic catalysis [94], and plasmonic gradient effects [95], and others. Similar on TERS, a new fluorescence technique, tip-enhanced fluorescence spectroscopy (TEFS), have been studied theoretically and experimentally recently [96–101]. With the combination of scanning probe microscopy (SPM), a very shape metallic SPM tip can generate a “hotspot” to strongly enhance several distinct photophysical sample responses including photo-induced light emission, electrically driven light emission and so on, as shown in Figure 12 [102].

In tip-enhanced near-field optical microscopy (TENOM), the conversion of free EM radiation with localised energy can be occurred with the help of the tip of TENOM. That is, the enhanced local EM field is excited with metallic tip, resulting in enhanced absorption of radiation, and the released of energy can be obtained by radiation efficiently. As a result, the tip in TENOM can be regarded as an optical antenna, which moderates the optical response of the target molecules by adjusting the excitation rate as well as the spontaneous emission rate. The general concept of fluorescence can be understood from section I. For the nano-shaped metallic tip configuration, the plasmon fluorescence enhancement factor is [101]

$$M_{Flu} = \left(\frac{\gamma_{exc}}{\gamma_0}\right)\left(\frac{Q}{Q_0}\right) = f^2\left(\frac{Q}{Q_0}\right)$$

In order to pursue high spatial resolution, the target molecules are often located near the metallic tip. As a result, the nonradiative energy transfer between the excited fluorophore and metal tip should be taken into account.

By adjusting the distance between the fluorophore and laser-irradiated AuNp, the distance-dependent fluorescence rate is investigated [103]. It is found that the continuous transition from enhanced fluorescence to quenched effect is observed experimentally, as shown in Figure 13. Theoretical analysis demonstrates that the local EM field is attributed to an increased excitation rate, while nonradiative energy transfer from molecules to AuNPs results in a decrease of the quantum yield (fluorescence quenched).

Furthermore, the strongly localised EM field provides a high spatial resolution for optical analysis (< 5 nm), which critically relies on the metal NP properties at the
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Figure 11: A) The scheme of IRDye Attached to gold nanorods, and steady-state fluorescence intensity of IRDye bound to gold nanorods as a function of silica shell thickness with plasmon band maxima located at B) 535 nm, C) 650 nm, D) 720 nm, E) 776 nm, and F) 823 nm. G) Two-tier contour plot of fluorescence intensity as a function of silica shell thickness and plasmon maximum [89].

Figure 12: Metal tip acted as a optical antennas with the enhanced effect: a) optical spectroscopy, b) photovoltaics, and c) electroluminescence [102].

apex of the metal tip [104]. And the near-field enhancement in the vicinity of the apex irradiated with illuminated EM field can be moderated by the tip sharpness. It was demonstrated that the excitation rate of fluorescence was strongly modulated by adjusting the distance between the metallic tip and the sample surface. A single photon fluorescence image with < 10 nm spatial resolution was obtained for the first time [98]. Excited by STM, the high vibrationally resolved fluorescence spectra from target molecule exhibit very good matches with the nor-

Figure 13: A) Sketch of the experimental arrangement. B) EM Field distribution (|E|^2, factor of 2 between successive contour lines) of fluorophore located nearby the substrate and faced with AuNP separated with 60 nm from the glass surface [103].
Figure 14: Tip-enhanced fluorescence images. A) Fluorescence demodulation signals. B) AFM probe height (5 nm at peak), C) Total photon count (TPC), D) blue curves shows TPC (×0.2) along the horizontal axis in (C) and red curves show the TPC within two ranges of tip-sample separation [98], and E) Fluorescence image of single Cy-3 molecules. Scale bar: 200 nm [99].

Figure 15: A) Molecular structure of H₂TBPP. B) STM image of molecular stacking at 50 pA and +2.5 V. C) Schematic of junction geometry with multimonolayer stacking [100].
6 PEF from rare-earth doped nanoparticle

Generally speaking, for infrared light excitation, rare-earth ions (Yb$^{3+}$) show small absorption cross-section, and exhibit very low energy transfer efficiency to Er$^{3+}$. Both of them restrict the potential application of UCNPs for biomedical imaging. It is reported that the luminescence-enhanced effect from Ln-doped NPs situated near noble metal nanostructures is generally attributed to the local enhanced EM field created among the metallic nanohole arrays, both the excitation and the radiative decay of UCNPs are moderated. It is found that the dramatic plasmonic enhancement of UC luminescence with 35-fold in Yb$^{3+}$ and Er$^{3+}$ co-doped NaYF$_4$ nanocrystals was observed at resonance condition [115]. The controllable UC fluorescence from co-doped nanorods (NaYF$_4$:Yb/Er/Gd) located at AuNPs arrays with different periodicities were also reported. It is found that the position of SPR and their local EM field intensity plays an important role in realizing the efficiency UC enhancement [116]. Furthermore, a gold pyramid pattern was also introduced to enhance the rate of resonant energy transfer from Yb$^{3+}$ to Er$^{3+}$ ions, and sixfold enhancement of the UCNP($\beta$-NaYF$_4$:Yb$^{3+}$/Er$^{3+}$) was obtained [117]. Zheng studied the robust DC and UC luminescence enhancement in lanthanide ions residing on silica hybrid nanostructures (LaF$_3$:Yb$^{3+}$, Er$^{3+}$@SiO$_2$) decorated with varying quantities of AgNPs [118]. By using an appropriate model for the fluorescence enhancement and the simultaneous quenching effects induced by the introduction of the plasmonic metallic nanostructure, the luminescence enhancement as a function of AgNPs loading with the rates of luminescence buildup and decay are observed. Recently, polyelectrolyte (PC) layers acting as a spacer to precisely control the distance between UCNPs and AuNPs was presented. At the best resonance condition between the UCNPs and AuNPs, a maximum fluorescence enhancement as high as 22.6-fold was obtained [119]. Compared with the conventional works reported about the UC, which are based on depositing nanocrystals on noble metallic nanostructure with various shaped aforementioned, Schietinger et al. presented the controlled PEF characteristic of UCNP (NaYF$_4$:Er$^{3+}$) via adjusting the distance between the particle and UCNP.
Figure 17: A) Schematic of the one dimensional RE-doped polymer RWG. B) AFM image of the TiO₂ RWG. c) UC fluorescence spectrum of a NaYF₄:Yb³⁺, Tm³⁺/PMMA thin film [114].

Figure 18: A) Schematic of the experimental setup. B) The scheme of the activator sensitizer system comprising Yb³⁺ and Er³⁺ ions in single nanocrystal [121].

by means of an AFM [120]. More recently, subdiffraction spatial resolution of tip-enhanced UC plasmon luminescence images of UC nanocrystals (NaYF₄:Er³⁺/Yb³⁺) on glass substrate was demonstrated, and it was found that plasmon enhanced UC efficiency critically depends upon the process of double photon excitation and HOMO energy transfer between ions located in the UCNP, as shown in Figure 18 [121].

7 Conclusions and outlook

SPR excited on metallic nanostructure’s surface provides very huge EM field enhancement by creating “hotspots”. As a result, placing the luminescent center near plasmonic nanostructure with resonances related to the fluorophore (absorption/emission frequencies) and tailoring and mas-
tering the local EM environment offers additional channels for luminescence enhancement over and above what occurs with smooth metal surfaces. In the review, we focused on recent advancements of PEF from inhomogeneous and homogeneous viewpoints. The most important factor of PEF is the distance between fluorophore and surface, and the tip-enhanced fluorescence effect, which determines enhanced or quenched effect of fluorescence. It is shown that the spectrum emission from the fluorophore located near the nanostructured metal surface can be modified by controlling the geometrical shape, composition of the nanostructure, and dielectric characteristics of the surrounding media. This review article described the controllable plasmon enhanced fluorescence of the target fluorophores with various nanosystems, which highlight the important role of PEF for the application of in point-of-care medical diagnostics, food control, and safety.

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