Purcell effect of nanoshell dimer on single molecule’s fluorescence

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Abstract: The Purcell effect of a nanoshell dimer on the fluorescence of a single molecule placed within the dimer’s gap is studied. The numerical results show that the nanoshell dimer acts as an antenna, making the energy transfer from an excited molecule to the dimer more efficient, and as a lowpass filter for the radiation of fluorescence to the far field. Moreover, the enhancement factor of a nanoshell dimer on the fluorescence is much higher than that of a solid Au dimer in the longer-wavelength regime.

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References and links

electric field intensity provided by the metallic nanostructure, but also on the apparent fluorescence quenching [28]. The effects depend not only on the strong local field through SPR effect including metallic particles [4, 5], nanorods [15], metallic tips [9, 11], core-shell nanoparticles [16, 17], nanoshells [18], nanodimers [19-24], nanoantennae [25], and bowtie-nanoantennae [26]. Although surface enhanced Raman scattering (SERS) [27] using metallic nanostructures has been successful for more than two decades, SEF was not until recently. Some experiments showed fluorescence enhancement [14, 15], while others showed fluorescence quenching [16, 17]. The effects depend not only on the strong local electric field intensity provided by the metallic nanostructure, but also on the apparent quantum yield of the molecule in the presence of the nanostructure. A two-stage model [9] of

1. Introduction

Purcell’s early work [1, 2] established that the spontaneous emission of an emitter can be influenced and modified by the environment. Recently, the Purcell effect of a metallic nanostructure on the fluorescence of a nearby molecule [3-13] has been extensively studied to determine how surface plasmon resonances (SPR) can enhance or quench the emission. The issue is of importance for applications in nano-optics, e.g. surface enhanced fluorescence (SEF) [14]. Several metallic nanostructures were proposed and studied for enhancing the local electric field through SPR effect including metallic particles [4, 5], nanorods [15], metallic tips [9-11], core-shell nanoparticles [16, 17], nanoshells [18], nanodimers [19-24], nanoantennae [25], and bowtie-nanoantennae [26]. Although surface enhanced Raman scattering (SERS) [27] using metallic nanostructures has been successful for more than two decades, SEF was not until recently. Some experiments showed fluorescence enhancement [13, 22], while others exhibited fluorescence quenching [28]. The effects depend not only on the strong local electric field intensity provided by the metallic nanostructure, but also on the apparent quantum yield of the molecule in the presence of the nanostructure. A two-stage model [9] of
the spontaneous emission process was proposed for analysis. The first stage, the excitation stage, is the excitation of the emitter; the second, the emission stage, is the emission of the excited molecule. This model allows us to identify and clarify the roles the metallic nanostructures play in each stage. In the excitation stage, the electric field in the vicinity of a metallic nanostructure is indeed dramatically intensified when irradiated by incident light, which is useful for exciting a nearby emitter. Once the molecule is excited, it behaves as an electric dipole to radiate the fluorescence. Förster energy transfer [2] between the dipole and the nanostructure occurs simultaneously, if the distance between the two is less than 100 nm. Because of the Ohm’s loss in the metal, the dissipation of the transferred energy will reduce the total radiation efficiency. The distance between the molecule and the metallic nanostructure is a key factor. A shorter distance always causes stronger absorption and dissipation by the metallic nanostructure, even though it also induces a stronger electric field to excite a neighboring molecule. Therefore the quenching of fluorescence by a nearby metal is usually observed, particularly when the distance is less than 3 nm, and the dipole’s orientation is parallel to the metal surface [28].

During the past decade, the nanoshell [18], a silica bead coated with an Au shell, was developed. It has the advantage of tuning the SPR band in the longer-wavelength regime, even in the near infrared, by controlling the thickness of Au shell. The metallic dimer [19-22] (a pair of close nanoparticles) has also attracted a lot of attention recently, because it provides a stronger electric field in the gap region than a single metallic nanoparticle does in its proximity. Some studies further showed that a nanoshell dimer [29-32] can provide a stronger local electric field than a single nanoshell and/or a solid Au dimer. Thus nanoshell dimers are potentially attractive for uses in SERS. However, the energy transfer between an excited molecule (an electric dipole) and a nanoshell dimer, and the efficiency of a dipole’s radiation in the presence of an adjacent nanoshell dimer during the emission need to be evaluated. Therefore, the purpose of this paper is to further investigate the overall enhancement of a nanoshell dimer on a single molecular fluorescence and to evaluate theoretically whether it is superior to the enhancement of a solid Au dimer for the applications of SEF. In order to study the overall effect of a nanoshell dimer on the fluorescence of a singular molecule, the multiple multi-pole (MMP) method [33, 34] is adopted to simulate the amplification of the local electric field of a nanoshell dimer irradiated by a plane wave for the excitation stage, and the apparent quantum yield of an electric dipole’s radiation in the presence of the dimer for the emission stage, respectively.

2. Model of nanoshell dimer on a single molecular fluorescence

Figure 1 shows the configuration of a nanoshell dimer (a pair of identical nanoshells) containing a molecule within the gap, where the radius of the silica core is denoted by \( r_0 \), the thickness of the Au shell by \( t \), and the gap by \( d \). The wavenumber vector of the incident plane EM wave is denoted by \( \mathbf{k} \). The molecule locates at the center of dimer which is also the origin of the coordinate system. When the molecule is excited, it is regarded as an electric dipole, and its unit orientation vector is \( \mathbf{e}_p \) with an angle \( \theta_p \) to the central line of the nanoshell dimer. In the following, the surrounding medium is assumed to be air, the core of the nanoshell is a silica bead with a relative permittivity of 2.1, and the frequency-dependent permittivity of Au [35] is used for analysis. Since there is no analytical solution for comparison, the convergence of MMP method is tested by comparing the results from different numbers of collocation points (1800 and 2400) distributed on the inner and outer surfaces of each nanoshell for the case of \( r_0 = 40 \) nm, \( t = 20 \) nm, \( \theta_p = 0^\circ \), \( d = 10 \) nm. The relative error is less than 0.5%.
3. Numerical results and discussion

For the excitation stage, the nanoshell dimer and the molecule are irradiated by an incident plane EM wave. The molecule is assumed to be unexcited at the beginning. Using the MMP method, the scattered and total fields of the nanoshell dimer irradiated by the plane wave are analyzed. The local-field factor is further calculated to evaluate the amplification of the electric field caused by the nanoshell dimer for exciting the molecule in this stage. The local-field factor, $K$, is defined as the normalized electric field at the position of the molecule by the amplitude of the electric field of the incident wave. For example, the local-field factor around a nanoshell dimer irradiated by a plane EM wave of $\lambda = 700$ nm and $k = e_x$ with a polarization along the central line of the dimer is depicted in Fig. 2(a), where the radius of the $\text{SiO}_2$ core is 40 nm, the thickness of the Au shell is 10 nm, and the gap is 10 nm. Within the gap region of the nanoshell dimer, a hotspot [29, 30] with a strong local electric field is observed. The phenomenon is due to the squeezing of the coupling SPR between the two adjacent nanoshells. This illustrates that a nanoshell dimer plays the role of a lens to focus the incident wave into a small hotspot region around the gap which size is much smaller than a wavelength, if the polarization of the incident plane wave is parallel to the dimer’s central line. Therefore, if a molecule is placed within the gap and if its excitation spectrum also covers this wavelength, it will then easily be excited to the excited state from the viewpoint of probability. However, if the polarization of the incident wave is perpendicular to the central line, there is no intensified electric field within the gap. This is because the coupling SPR effect of the two close nanoshells makes this structure possess a polarization-selective property to the incident wave.
Fig. 2. (a). Normalized electric field distribution in \( x-z \) plane around a nanosell dimer of \( r_0 = 40 \) nm, \( t = 10 \) nm, and \( d = 10 \) nm, which is irradiated by a plane wave with a polarization parallel to the dimer’s central line at \( \lambda = 700 \) nm. The scale in \( x \) (horizontal) and \( z \) (vertical) axes is nanometer. The local-field factor at the center of the gap is about 37. (b) Excitation rates at the center of the gap of a nanosell dimer with \( r_0 = 40 \) nm, \( t = 7,10 \) or 20 nm, and \( d = 20 \) or 10 nm irradiated by a plane wave with a polarization parallel to the dimer’s central line.

To analyze the behavior quantitatively, the excitation rate, \( |K|^2 \), is further studied. A typical case is considered; the molecule is at the center of the gap of the nanoshell dimer. The excitation rates versus wavelength for a nanoshell dimer (\( r_0 = 40 \) nm) with different thicknesses of Au shell (\( t = 7,10, 20 \) nm) are plotted in Fig. 2(b) for \( d = 20 \) nm and \( d = 10 \) nm respectively. These curves show that the frequency-dependent excitation rate depends sensitively on the thickness of Au shell and the gap. Normally, the smaller the gap, the stronger the excitation rate is [36]. It is also accompanied by a red shift in the spectrum [30]. In addition, the thinner the Au shell is, the more the red-shift of the SPR band will be for the excitation [18]. Moreover, the scattering cross section (SCS), the absorption cross section (ACS), and the extinction cross section (ECS) of Au nanoshell dimers (\( r_0 = 40 \) nm, and \( t = 7,10, 20 \) nm) interacting with the incident plane wave are calculated to exhibit their far-field responses, as shown in Fig. 3(a) for \( d = 20 \) nm and Fig. 3(b) for \( d = 10 \), where the polarization of the incident plane wave is parallel to the dimer’s central line. For comparison, these values (SCS, ACS, ECS) are normalized by the projection area of a single nanoshell, \( \pi (r_0 + t)^2 \). Comparing Fig. 2(b) with Fig. 3, we found that the far-field response of ECS is consistent with the near-field one of the excitation rate. The thinner the Au shell, the larger the ECS is and the more the red-shifts. However, a smaller gap does not increase SCS, ACS and ECS too much, even though it also induces little red shifts of these values.
Once excited, the molecule is modeled as an electric dipole for its subsequent emission. For this model, the MMP method is also used to simulate the interaction of a dipole with a nanoshell dimer. To assess the efficiency of the fluorescence emission under the influence of a nanoshell dimer, the radiative and nonradiative decay rates [37] of an electric dipole in the presence of a nanoshell dimer are further studied. The radiative decay rate represents the power emitted into the far field, while the nonradiative decay rate is the dissipating power in the metal. The surrounding medium is assumed to be lossless, e.g. air. The frequency-dependent results for a nanoshell dimer of \( r_0 = 40 \) nm with different thicknesses \((t = 7, 10, 20 \text{ nm})\) of Au shell containing a dipole at the center of the gap are depicted in Fig. 4(a) for \( d = 20 \) nm and 4(b) for \( d = 10 \) nm, where the dipole’s orientation is parallel to the central line \((\theta_p = 0^\circ)\).

These data are normalized by the radiative decay rate of a free dipole. These curves indicate that the nonradiative part dominates the emission over the radiative part in the shorter-wavelength regime (say < 600 nm), while the radiative part becomes dominant in the longer-wavelength regime. Both decay rates increase, as the gap decreases. In addition, when the Au shell becomes thinner, another peak of the nonradiative part in the longer-wavelength regime will also be induced, accompanying with the peak of the radiative decay rate. Therefore, if the Au shell is sufficiently thin, the nonradiative part dominates the whole...
Moreover, Figs. 4(a) and 4(b) indicate that the total normalized decay rate (the sum of the normalized radiative and nonradiative decay rates) of a dipole under the influence of a nanoshell dimer is much higher than that of a free dipole; i.e. the energy transfer between the dipole and the nanoshell dimer becomes more pronounced, as the gap decreases. Since the lifetime of the fluorescence is the inverse of the total decay rate of a molecule, Fig. 4 illustrates that the fluorescence lifetime will be shortened remarkably by the nanoshell dimer. Recent researches [38, 39] have demonstrated that the lifetimes of fluorophores can be reduced significantly by an adjacent metallic nanostructure. Our results show that the fluorescence lifetimes are reduced approximately by 3 orders of magnitude, depending on the gap size and the thickness of Au shell. Normally, the shorter the distance between the molecule and the metal is, the more severe the reduction in the fluorescence lifetime. The phenomenon shows that a nanoshell dimer plays the role of an antenna to provide an efficient energy-transfer channel between the dipole and the nanoshell dimer during emission.

Although the energy is easily transferred from the dipole to the nanoshell dimer, only a portion of the energy is allowed to radiate into the far field, while the rest is dissipated in the metal. The former is the radiative part, and the latter is the nonradiative part. The radiation efficiency is discussed by studying the apparent quantum yield $\eta$ of the whole system, $\eta = \Gamma_r / (\Gamma_r + \Gamma_{nr})$. The curves of $\eta$ versus wavelength for a nanoshell dimer ($r_0 = 40$ nm) with different thicknesses ($t = 7, 10, 20$ nm) of Au shell and different gaps ($d = 20, 10$ nm) are shown in Fig. 5(a) for $\theta_p = 0^\circ$. These results show that the smaller the gap is, the less the apparent quantum yield will be. In addition, a nanoshell dimer with a thinner Au shell has a less apparent quantum yield for $\theta_p = 0^\circ$. Moreover, the profile of the apparent quantum yield indicates that a nanoshell dimer acts as a lowpass filter for the emission of a vicinal dipole. For example, for the case of $t = 10$ nm and $d = 10$ nm, the cutoff wavelength of the lowpass filter is about 620 nm, as shown in Fig. 5(a). This is to say that only the photons of longer wavelength are allowed to radiate to the far field through the nanoshell dimer, but those of shorter wavelength are dissipated in the Au shell.

In contrast, if the dipole’s orientation is perpendicular to the dimer’s central line ($\theta_p = 90^\circ$), the apparent quantum yield becomes lower, as shown in Fig. 5(b); a nanoshell dimer with a thicker Au shell has a less apparent quantum yield. Summarily, the observed emission spectrum and lifetime of a molecule at the far field will be modified significantly by a nearby nanoshell dimer according to its orientation with respect to the central line of the dimer, from the viewpoint of Purcell effect.

![Image of apparent quantum yields](image-url)
Finally, to assess the overall Purcell effect of a nanoshell dimer on the fluorescence of a single molecule, the enhancement factor \( K^2(\lambda_{ex})\eta(\lambda_{em}) \) is used, where \( \lambda_{ex} \) and \( \lambda_{em} \) are the excitation and emission wavelengths respectively. According to the numerical results, we found that if the polarization of the incident plane wave is parallel to the central line of the nanoshell dimer, and the molecule is within the gap, the excitation rate is almost the maximum. If the orientation of the dipole is aligned with the central line (\( \theta_p = 0^\circ \)), the apparent quantum yield is the maximum. Therefore we restrict our analysis to the cases of a molecule (\( \theta_p = 0^\circ \)) placing at the center of a dimer. The enhancement factor \( K^2(\lambda)\eta(\lambda) \) is studied, under the assumption that there is no Stokes shift between the excitation and the emission spectra. The enhancement factors versus wavelength for nanoshell dimers (\( r_0 = 40 \text{ nm} \)) with different thicknesses of Au shell (\( t = 7, 10, 20 \text{ nm} \)) are depicted in Figs. 6(a) and 6(b) for \( d = 20 \text{ nm} \) and \( d = 10 \text{ nm} \), respectively.

For comparison, the results of a solid Au dimer (\( r = 50 \text{ nm} \)) are also plotted. These curves show the overall enhancement of a nanoshell dimer on the fluorescence is much higher than that of a solid Au dimer in the longer-wavelength regime. In addition, the enhancement factor for the \( d = 10 \text{ nm} \) dimer is stronger than that of \( d = 20 \text{ nm} \). However, when the gap is less than 6 nm, the enhancement factor will decrease dramatically, due to a very low apparent quantum yield. Moreover, it seems the thinner the Au shell, the stronger the enhancement factor in the longer-wavelength regime is. However, there is an optimum thickness of Au shell to obtain a maximum enhancement factor according to our other results. For example, the optimum thickness is 5 nm for the case of \( d = 20 \text{ nm} \), and the corresponding maximum enhancement factor is 400 at \( \lambda = 800 \text{ nm} \). If the thickness is thinner than the optimum value, the maximum enhancement factor still red-shifts, but its value decreases since the increase of the nonradiative part will reduce the apparent quantum yield. Generally, the enhancement factor of a nanoshell dimer on a single molecule’s fluorescence can reach factors of about 800, if the gap is as small as 10 nm, the thickness of Au shell is as thin as 10 nm, and the excitation and emission spectra of the molecule are between 720 – 680 nm. In other words, a nanoshell dimer is not suitable for the enhancement of molecular fluorescence, whose emission spectrum is in the blue to green regime of the visible spectrum.

4. Conclusion

The Purcell effects of a nanoshell dimer on a single molecule’s fluorescence were discussed from two aspects. Although a nanoshell dimer behaves as a lens to collect and focus the
shining light into the gap region for exciting a molecule within this area, it also acts as an antenna making the Förster energy transfer from the excited molecule (an electric dipole) to itself efficient. In addition, it acts as a lowpass filter for the emission allowing most of the longer-wavelength photons radiate to the far field, but dissipating the shorter-wavelength part into Joule’s heat. Consequently, the total radiative decay rate of an excited molecule becomes remarkably high under the influence of the nanoshell dimer, so that the lifetime of the fluorescence will be reduced by three orders of magnitude. Summarily, the overall enhancement of a nanoshell dimer on the fluorescence is much higher than a solid Au dimer in a longer-wavelength regime, if the polarization of the shining light, the molecular orientation, and the central line of dimer are parallel to each other.

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