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Enhancing photoluminescence of Au – TiO_2 nanoparticles using Drude model

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Abstract

The enhancement of photoluminescence of Au-TiO_2 nanoparticles by surface plasmon resonance has been studied extensively by experiment in recent years. For the purpose of optimizing the photoluminescence property of Au-TiO_2 nanoparticles, the manufacturing parameters related to the Au nanoparticles and TiO_2 nanoparticles need to be considered. In this paper, Drude model and Maier's effective volume method are used to analyze the variation of the metal nanoparticle radius, separation between metal nanoparticle and dielectric molecule, and total absorption cross-section with original radiative efficiency on the photoluminescence property of Au-TiO_2 nanoparticles. The results show that to obtain the optimized enhancement factor for photoluminescence process, the size of Au nanoparticle is about $13-20\ nm$, the separation between Au nanoparticle and TiO_2 molecule is about $5-15\ nm$, the total absorption cross-section of TiO_2 molecules is about $1-100\ nm^2$ and the original radiative efficiency of TiO_2 molecule is weak about $0.001-0.1$. With these fabrication parameters, the photoluminescence property of Au-TiO_2 nanoparticles can be enhanced several thousand times compared to traditional TiO_2 nanoparticles.

Key words: surface plasmon resonance, photoluminescence, Drude model, Maier effective volume method, Au- TiO_2.

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I. Introduction

The enhancement of photoluminescence (PL) from dielectric molecules located in the proximity of rare metal nanoparticles such as gold (Au), silver (Ag), copper (Cu), … is particularly interested [1 – 3]. Unlike Ag and Cu, Au is not oxygenated in different environments so it is widely used. Depending on using or researching, Au is embedded into a compatible medium such as TiO_2, ZnO, GaN, … [4 – 9].

Incorporating Au nanoparticles into TiO_2 dielectric material enables the absorption of light to expand from visible to near–infrared light and to enhance the photovoltaic conversion by Surface Plasmon Resonance (SPR) [10, 11]. The enhancement of optical properties of Au nanoparticles embedded into TiO_2 have been confirmed by experimental investigations [10, 12 – 14] but theoretical studies on this problem are limited. The most important theoretical investigations are papers of G. Sun et al. [15 – 17].

G. Sun et al. employed Drude model and Maier's effective volume method to develop a theoretical model of the enhancement of photoluminescence of dielectric molecules in the vicinity of metal nanoparticles in the case of considering radiative decay of surface plasmon. These papers have received a lot of attention of physicists who specialize in plasmons, fluorescence, and emission for applications in the field of the diode, sensor, … [18 – 20].

In this paper, following the research by G. Sun, we investigated the effect of Au nanoparticles on the photoluminescence property of the Au–TiO_2 nanoparticles by calculating PL enhancement factor and optimizing this factor. The PL enhancement factor depends on parameters such as the Au nanoparticle radius, the separation between Au nanoparticles and TiO_2 molecules, the total absorption cross–section and the original radiative efficiency of TiO_2 molecule, we gave the suggestions to select the appropriate value of these parameters to enhance the photoluminescence property.

II. Theoretical model

An Au nanoparticle with the dielectric constant ω_M and the radius r is embedded into the dielectric medium with the dielectric constant ε_D and is separated to a TiO_2 molecule about d as shown in Fig 1. Each Au nanoparticle simultaneously has a lot of charge distribution and generates many different electric multipole moments (modes). However, due to the good coupling between dipole mode and external radiation fields, we are only interested in the effects of dipole mode on the enhancement of photoluminescence. Therefore, to eliminate the effect of higher modes, we calculated the PL enhancement factor from the separation $d \geq 5\ nm$ for the Au–TiO_2 nanoparticles.

The process of PL enhancement consists of two mechanisms. When the beams of excited light, which

have the frequency ω_{ex}, converged on the area of Au–TiO_2 nanoparticles, the excited light beams will couple with the dipole modes of Au nanoparticles to generate energy. Then, these energy will be absorbed by the TiO_2 molecules, radiative decayed and the non–radiative decayed. The energies of the TiO_2 molecules will be partly reduced by lattice vibrations, heat transfer, … and the rest is radiated back to the dipole mode in frequency ω_{PL}. Therefore, the PL enhancement process consists of optical absorption and emission. It is clear that $\omega_{ex} \geq \omega_{dp} \geq \omega_{PL}$ is always satisfied, where ω_{dp} is the dipole frequency [15]. When the appearance of resonance $\omega_{ex} = \omega_{dp} = \omega_{PL}$, this process becomes stronger, so, PL enhancement factor increases significantly.

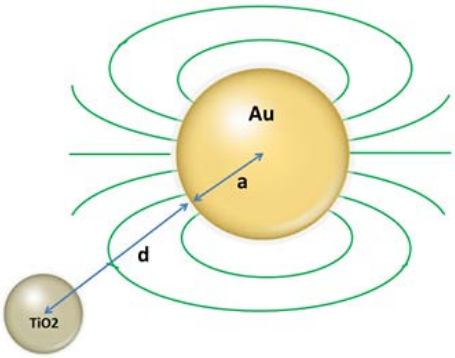

Fig 1. An Au nanoparticle with the dielectric

constant ω_M and the radius r is embedded into the dielectric medium with the dielectric constant ε_D and is separated to a TiO_2 molecule about d.

The PL enhancement factor when the resonance occurs is [15]

$$F_{PL}(\omega_{dp}) = F_{ABS}(\omega_{dp}) F_{EL}(\omega_{dp}). \qquad (1)$$

The PL enhancement factor F_{PL} depends on the absorption enhancement factor F_{ABS} and the electroluminescence enhancement factor F_{EL}.

The expression of the absorption enhancement factor when resonance occurs is [15]

$$F_{ABS}(\omega_{dp}) = \frac{9\varepsilon_D}{4}\left(\chi^3 + Q_n^{-1} + Q_a^{-1}\right)^{-2}\left(1+\frac{\chi_d}{\chi}\right)^{-6}, \qquad (2)$$

where $\omega_{dp} = \frac{\omega_p}{\sqrt{1+2\varepsilon_D}}$ is the resonant frequency, $\chi = \frac{2\pi a}{\lambda_{dp}}$ is the normalized radius, $\chi_d = \frac{2\pi d}{\lambda_{dp}}$ is the normalized separation, $Q_n \approx \frac{2\omega_{dp}}{\gamma(1+2\varepsilon_D)}$ is the non–radiative decay factor and $Q_a \approx \frac{\chi^3 \lambda_{dp}^2}{3\pi\varepsilon_D N_a \sigma_a}\left(1+\frac{\chi_d}{\chi}\right)^6$ is the absorption decay factor. In the formula of ω_{dp}, $\omega_p = 8.45\ eV$ is the plasma frequency of Au nanoparticles [15], $\varepsilon_D = 6.2$ is the dielectric constant of TiO_2 [21]. From there, we calculated $\omega_{dp} = 2.31\ eV$. In the formula of Q_n, $h\gamma = 0.045\ eV$ is the loss in Au [22]. In the expression of Q_a, $\lambda_{dp} = \frac{2\pi c}{\varepsilon_D^{1/2}\omega_{dp}} \approx 215\ nm$ is the dipole wavelength of Au. Thus, the absorption enhancement factor F_{ABS} is a function depends on the radius r of Au nanoparticles, the separation d from Au nanoparticle to TiO_2 molecule, and the total absorption cross–section $N_a\sigma_a$ of TiO_2 molecules. Each optimized Au radius, the separation d and the cross–section $N_a\sigma_a$, we determined the value of the optimized absorption enhancement factor is

$$F_{ABS,opt}(\omega_{dp}) = \frac{9\varepsilon_D}{4}\left(1+\frac{d}{a_{ABS,opt}}\right)^{-6}\left[2\left(\frac{3\pi\varepsilon_D N_a\sigma_a}{\lambda_{dp}^2}\right)^{1/2} + \frac{\gamma(1+2\varepsilon_D)}{2\omega_{dp}}\right]^{-2} \qquad (3)$$

The electroluminesce enhancement factor when resonance occurs is [5]

$$F_{EL}(\omega_{dp}) = \frac{1+F_{p,1}(\omega_{dp})\eta_{dp}}{1+F_{p,1}(\omega_{dp})\eta_{rad}}, \qquad (4)$$

in which $F_{p,1}(\omega_{dp})$ is Purcell factor of the dipole mode, η_{rad} is the original radiative efficiency of TiO_2 when Au nanoparticles are not loaded and η_{dp} is the radiative coupling efficiency of the dipole mode. Purcell factor of the dipole modes when resonance occurs is [15]

$$F_{p,1}(\omega_{dp}) = \frac{9\varepsilon_D}{2\chi^3}\left(\chi^3 + Q_n^{-1}\right)^{-1}\left(1+\frac{\chi_d}{\chi}\right)^{-6}, \qquad (5)$$

and the radiative coupling efficiency of the dipole modes is [15]

$$\eta_{dp} = \left(1+\frac{\gamma_{nrad}}{\gamma_{rad}}\right)^{-1} = 1+\left(Q_n\chi^3\right)^{-1}. \qquad (6)$$

So, the electroluminescence enhancement factor is a function of the radius r, the separation d, and the efficiency η_{rad}.

Totally, F_{PL} depends on the radius r, the separation d, the cross-section $N_a\sigma_a$ and the efficiency η_{rad}.

III. Results and discuss

In theory, the PL enhancement factor F_{PL} depends on the radius r, the separation d, the cross-section $N_a\sigma_a$ and the efficiency η_{rad}. Herein, we performed F_{PL} factor by fixed two parameters and showed the radius r in some of the remaining parameter values as shown in Fig 2.

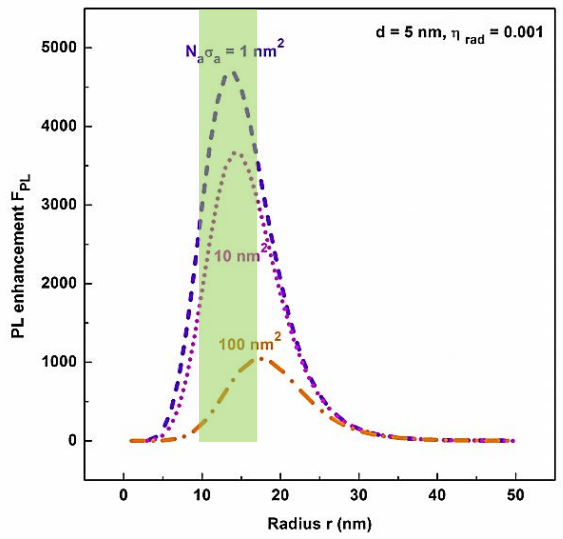

Fig 2. The graph of PL enhancement factor on the radius r of Au nanoparticle with separation $d = 5\ nm$, original radiative efficiency $\eta_{rad} = 0.001$ on some values of total absorption cross-section $N_a\sigma_a$.

In Fig 2, we found that the curves of F_{PL} factor increase on the radius r when fixed at $d = 5\ nm$, $\eta_{rad} = 0.001$ with three different $N_a\sigma_a$ values, factor F_{PL} increases to a maximum value then decreases

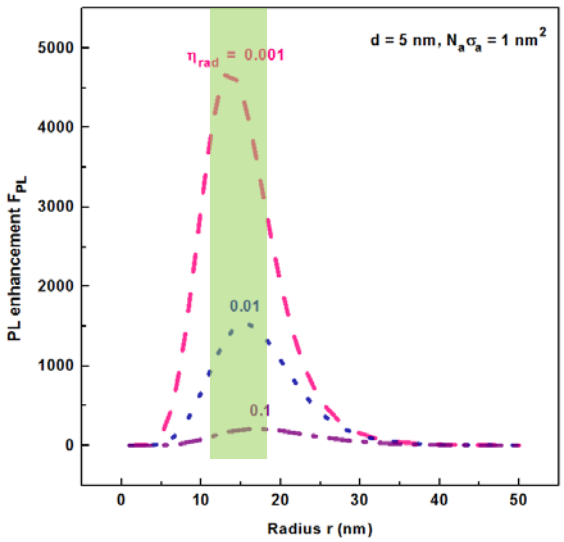

Fig 3. The graph of PL enhancement factor on the radius r of Au nanoparticle with the separation $d = 5\ nm$, the total absorption cross-section $N_a\sigma_a = 1\ nm^2$ on some values of the original radiative efficiency η_{rad}.

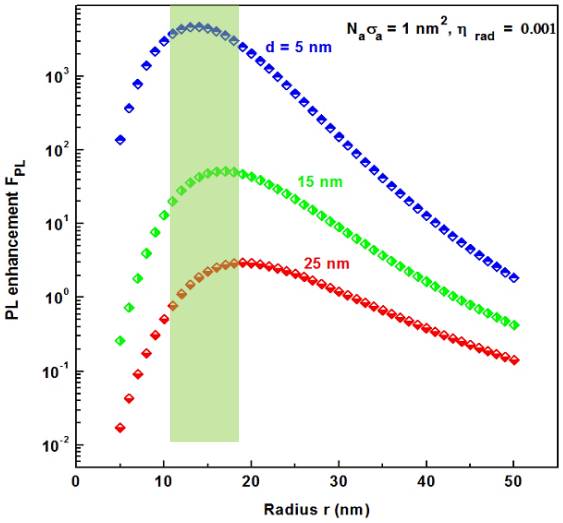

Fig 4. The graph of PL enhancement factor on the radius r of Au nanoparticle with the total absorption cross-section $N_a\sigma_a = 1\,nm^2$, the original radiative efficiency $\eta_{rad} = 0.001$ on some values of separation d between Au nanoparticle with TiO_2 molecule.

sharply to 0. When the cross-section $N_a\sigma_a$ increases, F_{PL} factor falls gradually. For each value of $N_a\sigma_a$, F_{PL} has a value close to 0 when the radius is greater than $30\,nm$. Henceafter, we should not produce Au nanoparticles with radii larger than $30\,nm$ in applications requiring high photoluminescence for Au–TiO_2 nanoparticles. In Fig 3, for each value of efficiency η_{rad}, factor F_{PL} falls dramatically. For $\eta_{rad} = 0.1$, F_{PL} seems too small. Like Fig 2, when the radius is greater than $30\,nm$, the value of F_{PL} is near 0. For Fig 4, when separation d increases, factor F_{PL} decreases spectacularly. The maximum value of F_{PL} corresponding to each value r is in the range $13-20\,nm$. In summary, separation d or cross-section $N_a\sigma_a$ or efficiency η_{rad} rises, F_{PL} factor falls, in which, when d increases, F_{PL} will fall most then η_{rad} and finally $N_a\sigma_a$. Therefore, in order to PL process to be strengthened, one should ensure that the separation between Au nanoparticle with TiO_2 molecule and original radiative efficiency are small. Moreover, one should not fabricate Au nanoparticles with radii of $30\,nm$ or more.

For each optimized radius of Au nanoparticles, the optimized PL enhancement factor $F_{PL,opt}$ is a function of the separation d, the cross-section $N_a\sigma_a$ and the efficiency η_{rad}. Because factor $F_{PL,opt}$ is a function of three parameters, we cannot perform a graph of this factor depends on the parameters by three – dimensional graph. On the other hand, to easily visualize, we have performed a graph of factor $F_{PL,opt}$ depends on the cross-section $N_a\sigma_a$ by fixing $\eta_{rad} = 0.001$ and an other graph of factor $F_{PL,opt}$ depends on the efficiency η_{rad} by fixing $N_a\sigma_a = 1\,nm^2$ with some values of separation d. In general, the curves of factor $F_{PL,opt}$ are reduced. In Fig 5, when the cross-section $N_a\sigma_a$ has a value from $1-100\,nm^2$,

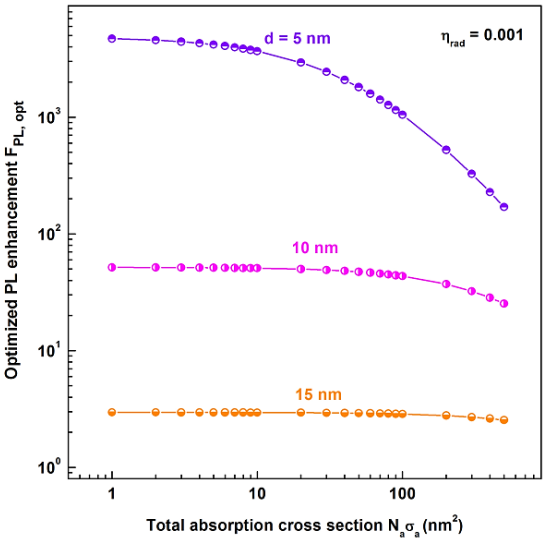

Fig 5. The optimized PL enhancement factor $F_{PL,opt}$ on the total absorption cross-section $N_a\sigma_a$ by fixing the original radiative efficiency $\eta_{rad}=0.001$ with some values of the separation d between Au nanoparticle with TiO_2 molecule.

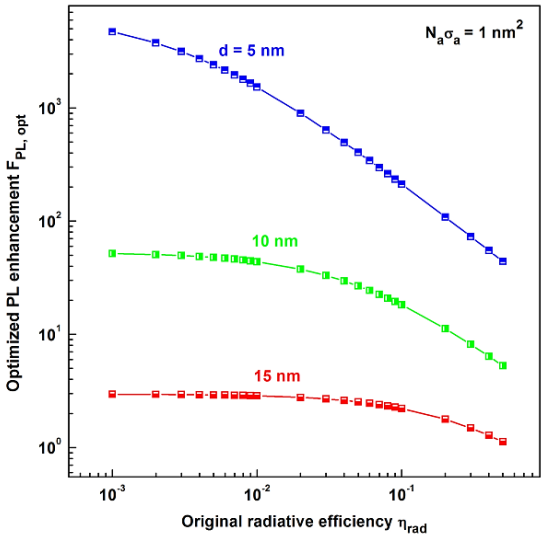

Fig 6. The optimized PL enhancement factor $F_{PL,opt}$ on the original radiative efficiency η_{rad} by fixing the total absorption cross-section $N_a\sigma_a=1\,nm^2$ with some values of the separation d between Au nanoparticle with TiO_2 molecule.

factor $F_{PL,opt}$ falls slightly, when $N_a\sigma_a$ is greater than $100\,nm^2$, $F_{PL,opt}$ falls modestly and when $N_a\sigma_a$ continues to increase, then $F_{PL,opt}$ approaches zero. The separation d increases too much, $F_{PL,opt}$ almost unchanges on $N_a\sigma_a$. In Fig 6, when the efficiency η_{rad} boosts in the case the separation d is small, factor $F_{Pl,opt}$ decreases rapidly; as d increases, $F_{PL,opt}$ falls marginally. Consequently, the PL enhancement factor is optimized when some molecules, which have small absorption cross-section and original radiative efficiency, are placed near metal nanoparticles.

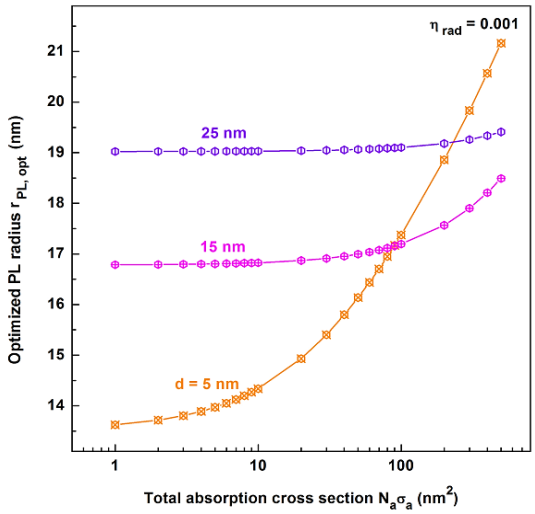

Fig 7. The optimized radius of Au nanoparticle $r_{PL,opt}$ at PL enhancement factor is maximum on the total absorption cross-section $N_a\sigma_a$ with the original radiative efficiency $\eta_{rad}=0.001$ some values of separation d between Au nanoparticle and TiO_2 molecule.

To gain factor $F_{PL,opt}$ for each value of the separation d, the cross-section $N_a\sigma_a$, and the efficiency η_{rad}, the radius of Au nanoparticle must be optimized $r_{PL,opt}$. Fig 7 shows the optimized radius $r_{PL,opt}$ depending on the cross-section $N_a\sigma_a$ and Fig 8 shows the optimized radius $r_{PL,opt}$ depending on the original radiative efficiency η_{rad}. In general, the curves of $r_{PL,opt}$ are quite complex. Thus, similar to the above, one

wants to get factor $F_{PL,opt}$ of great value, the separation between Au nanoparticle and TiO_2 molecule is about $5-15\,nm$, the absorption cross-section of TiO_2 molecules is between $1-100\,nm^2$ and the original radiative efficiency of TiO_2 molecule is weak between $0.001-0.1$, so the radius must be within the range $13-20\,nm$.

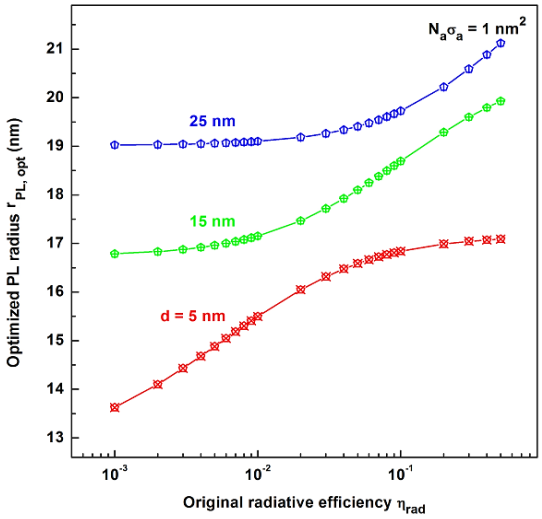

Fig 8. The optimized radius of Au nanoparticle $r_{PL,opt}$ at PL enhancement factor is maximum on the original radiative efficiency η_{rad} with the total absorption cross-section $N_a\sigma_a = 1\,nm^2$ some values of the separation between Au nanoparticle and TiO_2 molecule.

III. Conclusions

In this report, Drude model and Maier's effective volume method are used to show the enhanced photoluminescence factor as well as the optimization of this factor on Au nanoparticle radius, the separation between Au nanoparticle with TiO_2 molecule, the total absorption cross-section and the original radiative efficiency based on Au-TiO_2 nanoparticles. The results show that to obtain the optimized enhancement factor for photoluminescence process, we need to fabricate Au nanoparticles, which have the sizes of $13-20\,nm$, separated from TiO_2 molecule about $5-15\,nm$, the absorption cross-section of TiO_2 molecules or the density of TiO_2 molecules on an Au nanoparticle is small enough to make total absorption cross-section between $1-100\,nm^2$ and original radiative efficiency of TiO_2 molecule is weak between $0.001-0.1$.

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