Optik 124 (2013) 1338–1341

Contents lists available at SciVerse ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Using Au/SiO_2 core–shell structure to enhance the fluorescence of MEH-PPV in the detection of nitrated aromatic explosives

Fenghong Chu[a,*], Yage Zhan[b], Junjie Yang[a], Jiyuan Wang[a]

[a] Shanghai University of Electric Power, Shanghai 200090, China
[b] Donghua University, Shanghai 201602, China

ARTICLE INFO

Article history:
Received 2 November 2011
Accepted 17 March 2012

Keywords:
Metal-enhanced fluorescence
Dye
Surface energy transfer

ABSTRACT

Au/SiO_2 core–shell structure is used to enhance the fluorescence of MEH-PPV in the detection of nitrated aromatic explosives. The fluorescence intensity of MEH-PPV can be influenced by locally enhancing the excitation intensity, by increasing the emitter's radiate rate, and decreasing its fluorescence intensity by surface energy transfer (SET). Theoretical calculation results show that by modulate Au/SiO_2 core–shell structure the optical properties of MEH-PPV could be tunable. With increasing the gold core radius and decreasing the shell thickness always leads the local field enhancement factor increases. However the optimal shell thickness is found to be a trade-off between radiate decay rate and surface energy transfer. From the analytic it can also be concluded that the silica shell with dielectric constant of 1.42 is a perfect choice.

1. Introduction

Explosives and explosive-like compounds are important in many diverse fields. Detection of these materials is necessary in a variety of complex environments, including mine fields, munitions storage facilities, wastewater treatment facilities, transportation areas, and blast sites. In each of these settings, sensitive and timely detection of explosive materials is necessary to ensure the safety and security of the surrounding area [1].

Nitrated aromatic explosives are non fluorescent in nature, but these molecules can quench the fluorescence of some of the dye. Fluorescence-quenching based sensing has gained increasing interest in detection of explosives because of its sensitivity, selectivity and simplicity. Various organic molecules and polymers have been fabricated into thin films or porous materials and used in explosives sensing [2–5]. However, the fluorescence intensity of most conjugated polymers and organic molecules, particularly dyes, used thus far in fluorescence sensing are too weak to detect. Method must take to increase the reliability and thus minimize the false positives in explosives identification. The use of nanoparticle technology to overcome the limitations of classical dye probes has increased in recent years [6–9].

It has been proved that fluorescence can be quenched when the dye is in close proximity to a metal particle, but enhanced when the dye is separated by a certain distance. Such fluorescence enhancement phenomenon is defined as metal-enhanced fluorescence (MEF). MEF is based on the interactions of the excited state dye with the plasmon resonance of a metal particle and the enhancement scale depends on the particle size, shape and the distance between the dye molecule and the metal particle. MEF can increase the quantum yield and stability, reduce the lifetime of fluorescence and broaden the transfer distance of fluorescence resonance energy transfer. MEF is a useful technology and has been widely applied to increase the detection sensitivity of target molecule in biological assay [10].

In recent years, considerable effort has been devoted to the design and controlled fabrication of core–shell structured nanoparticles. Metal nanoshells exhibit a geometric tenability, the optical and electric properties from these nanoparticles will be altered and controlled. In this work, Au/SiO_2 core–shell structure was used to enhance the fluorescence of MEH-PPV in the detection of nitrated aromatic explosives. The silica shells not only enhance the colloidal stability but also control the distance between core particles with dye through shell thickness. The fluorescence emission of dye can be enhanced by properly tailoring its photonic environment. The environment can affect the fluorescence emission in three ways: (i) by locally enhancing the excitation intensity, (ii) by increasing the emitter's radiate rate, and (iii) decreasing its fluorescence intensity by surface energy transfer (SET). In this paper the overall performance of Au/SiO_2 core–shell on the fluorescence of MEH-PPV is studied theoretically.

* Corresponding author. Tel.: +86 021 68029203; fax: +86 021 68029203.
E-mail address: chufenghong@siom.ac.cn (F. Chu).

0030-4026/$ – see front matter © 2012 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2012.03.070

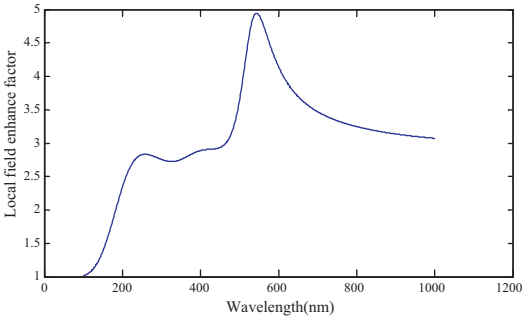

Fig. 1. Plot of local field enhancement factor of gold nanoparticles as a function of wavelength for pure gold nanospheres with radius of 20 nm.

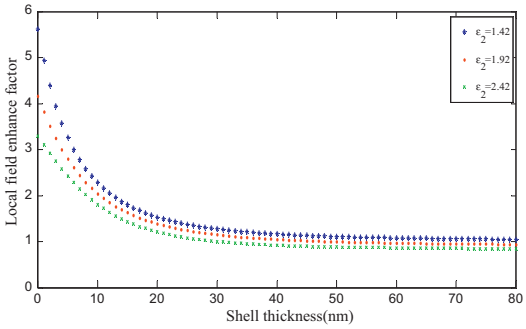

Fig. 3. Plot of local field enhancement factor in the dielectric shell with different dielectric shell constant ε_2, $r_1 = 20$ nm, $\varepsilon_3 = 1.5$, wavelength = 543 nm.

2. Theories, calculations and discussions

2.1. Enhancing the fluorescence intensity of MEH-PPV by locally enhancing the excitation intensity

Local field enhancement of metallic nanostructures is an intriguing phenomenon which can enhance the excitation intensity. The metal core has radius r_1 and frequency-dependent dielectric function ε_1 [11], the silica shell has a thickness $r_2 - r_1$ and dielectric constant ε_2, the embedding dye medium has dielectric constant ε_3, in this article the embedding dye is MEH-PPV with dielectric constant of 1.5. Based on quasi-static theory [12], the local field enhancement factor R at the exterior surface of the silica shell (the electric field ratio between the electric field at the exterior surface of the silica shell E_e and the applied field E_0, i.e. E_e/E_0) can been written as [12]:

$$R = \left|\frac{E_e}{E_0}\right| = \frac{3\varepsilon_3[\varepsilon_1 + 2\varepsilon_2 + 2(\varepsilon_1 - \varepsilon_2)(1-p)]}{3\varepsilon_2(\varepsilon_1 + 2\varepsilon_3) + 2p[(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 - \varepsilon_3)]} \quad (1)$$

where $p = 1 - (r_1/r_2)^3$.

It is shown in Fig. 1 that the local field enhancement factor peaks takes place at about 252 nm and 543 nm, which is close to the SPR band of spherical gold nanoparticles.

The calculated contour plot of local field enhancement factor is plotted in Fig. 2 for different silica shell thickness while the gold core diameter is fixed to a value of 20 nm. When coated with silica shell (corresponding dielectric constant $\varepsilon_2 = 1.42$), the maximum of local field enhancement factor at exterior surface of the shell red shifts from 543 nm to 546 nm with increasing the shell thickness from 0 to 10 nm. However, increasing the shell thickness always leads the intensity of the local field enhancement factor decreases.

The difference between shell and surrounding medium dielectric constant also plays an important role to impact the performance of the Au/SiO_2 core–shell structure. From Fig. 3 we can see that when coated with silica shell with dielectric constant of 1.42 which is lower than the embedding dye medium dielectric constant, the local field enhancement factor is 5.6 when the shell thickness is zero. Increasing the shell dielectric constant will lead the local field enhancement factor getting smaller. For example, when the shell dielectric is 1.92 (or 2.42) the local field enhancement factor is 4.1 (or 3.2) when the shell thickness is zero. Furthermore, the intensity changing speed become slower and slower and approach to a constant when the shell thickness is two times of the radius of the gold core. From the above analytic it can be concluded that the silica shell is a perfect choice.

The local field enhancement characteristics in Au/SiO_2 nanoparticles depend also on the metal particle size. Fig. 4 shows that increasing the gold core radius will lead the local field enhancement factor getting larger. A maximum enhancement of the local field enhancement factor is observed at a size of 100 nm with silica shell, when the core radius is larger than 100 nm the local field enhancement factor keeps stable. For a particle gold core radius the performance of the Au/SiO_2 nanoparticles with smaller shell dielectric constant is better than the larger one.

All these studies show that the local field enhancement around gold nanoparticles becomes controllable by carefully altering the dielectric shell thickness, the dielectric constant of the shell and gold core radius.

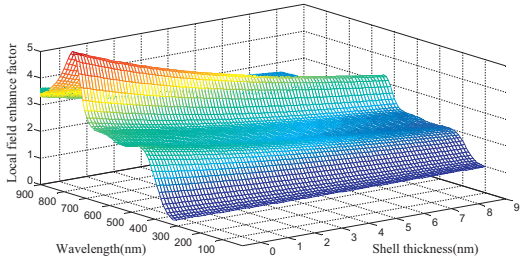

Fig. 2. 3D plot of local field enhancement factor of Au/SiO_2 core–shell structure as a function of wavelength and shell thickness. $r_1 = 20$ nm, $\varepsilon_2 = 1.42$, $\varepsilon_3 = 1.5$.

2.2. Enhancing the fluorescence intensity of MEH-PPV by increasing the emitter's radiate rate

It has been demonstrated in many different situations that the spontaneous emission rate of a single emitter depends on the environment [13]. The radiate rate of molecules close to metallic surfaces can increase and this can enhance the fluorescence of

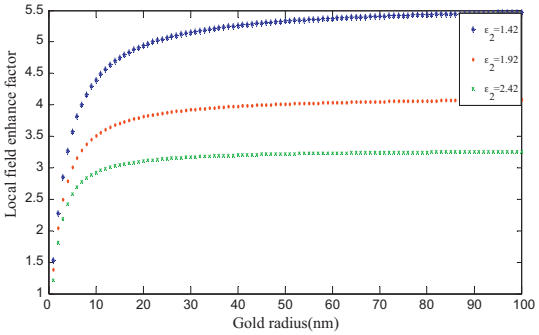

Fig. 4. Plot of local field enhancement factor of Au/SiO_2 core–shell structure as a function of gold radius with different dielectric constant ε_2, shell thickness = 1 nm, $\varepsilon_3 = 1.5$, wavelength = 543 nm.