Journal of Luminescence 173 (2016) 199–202

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Fano-induced spontaneous emission enhancement of molecule placed in a cluster of asymmetrically-arranged metallic nanoparticles

Khai Q. Le [a,b,*], Jing Bai [b], H.P.T. Nguyen [c]

[a] Faculty of Science and Technology, Hoa Sen University, Ho Chi Minh, Vietnam
[b] Department of Electrical Engineering, University of Minnesota, Duluth, MN 55812, USA
[c] Department of Electrical and Computer Engineering, New Jersey Institute of Technology, NJ 07102, USA

ARTICLE INFO

Article history:
Received 25 March 2015
Received in revised form
7 January 2016
Accepted 13 January 2016
Available online 19 January 2016

Keywords:
Plasmon enhanced spontaneous emission
Fano resonance
Plasmonic Metamolecules

ABSTRACT

We demonstrate that plasmonic Fano resonance significantly boosts spontaneous emission rate of a single emitter, *e.g.* atom, molecule and quantum dot, over a moderately broad emission spectrum. An emission enhancement of up to 140 times compared to the system with no external inclusion at tunable frequencies is achieved, providing a new complementary enhancement mechanism. Fano resonance is induced in clusters of four asymmetric-arranged nanoparticles with ultra-small inter-particle gaps. It is shown to play a dominant role in light-emitting enhancement, mediated by combined localized surface plasmon resonances.

1. Introduction

Spontaneous emission rate (SER) of a single emitter can be amplified by resonant coupling to surrounding media. Such a photon emission can be manipulated by the radiative decay rate of the emitting molecule [1]. As the single emitter is coupled to external objects such as resonant cavities [2,3], photonic crystals [4–6], semiconductor quantum wells [7–9], metallic nanoparticles and surface/multilayer metal structures [10–20] and many others [21–24], its spontaneous radiative emission rate is dramatically enhanced. Among those resonant cavity structures, metallic nanoparticles have been intensively studied due to their ability to strongly enhance the emitting molecule's SER, particularly, when the molecule is properly placed in close proximity to their structural surfaces. This anomalous enhancement, measured by means of the Purcell factor [1], is a consequence of matching between the localized surface plasmon resonance (LSPR) frequency and the molecule's emission spectrum. Several practical applications based on this enhancement mechanism have been realized including plasmonic enhancement of light emitting diodes [25–27], photonic crystal lasers [28] and photon up-conversion for boosting solar energy conversion efficiency [29–32]. Plasmonic effects on the photon emission of nearby molecules can be described as (i) amplification of radiative decay rate of the molecule and (ii) modification of the coupling efficiency of the emitting photon to the far-field *via* nanoparticle scattering [33]. These effects can be manipulated by size, shape, distribution of nanoparticles, and distance between the emitting molecule and the cluster of nanoparticles since the optical response is very sensitive to structural parameters.

The photon emission can be significantly enhanced as the emitting molecule is placed in close proximity to the nanoparticle at a distance of a few nanometers [34,35]. However, at certain small distances the emission may be quenched [36,37] since the emission mechanism is influenced by the balance between radiative (corresponding to the photon emission) and nonradiative decay rate (corresponding to the energy dissipation) [38]. The quenching and enhancement occur in different distance ranges. Therefore, proper tailoring of the emitter–nanoparticle separation plays a crucial role in boosting its SER and radiative decay rate efficiency. In particular, as the LSPR mode matches with the emission mode of interest, the strongest emission enhancement can be achieved. However, this mode matching is available only for a narrow bandwidth of operation due to a plasmonic nature of constituent nanoparticle materials that may hinder its potential applications. Clustering of nanoparticles can generate multiple resonance modes, which could broaden the enhanced emission spectrum [39–41]. Engineering the dispersion relation of artificial materials, *e.g.* hyperbolic metamaterials (HMMs), can also result in a broadband emission enhancement of nearby emitters [21]. Although nano-patterning hyperbolic metamaterials provides an efficient alternative to enhance the nearby molecule's emission spectrum over a broad band of frequencies, the Purcell factor remains relatively low [21,22]. The emission enhancement is based

* Corresponding author at: Faculty of Science and Technology, Hoa Sen University, Ho Chi Minh, Vietnam.
E-mail address: khai.lequang@hoasen.edu.vn (K.Q. Le).

http://dx.doi.org/10.1016/j.jlumin.2016.01.021
0022-2313/

on the outcoupling of non-radiative plasmonic modes of nano-patterned HMMs with an emitter [21]. In this work, we introduce an alternative mechanism associated with plasmonic Fano resonances to provide additional complementary enhancement and a broader bandwidth of emission.

The Fano-induced enhancement concept has been successfully employed for boosting absorption efficiency of organic photovoltaic cells [42]. In combination to conventional LSPRs, Fano resonances produce collections of strong resonances associated with large field enhancement to increase light absorption over a broad bandwidth of operation. The excitation of Fano resonances was carried out in clusters of four nanoparticles with asymmetric positioning and small inter-particle gaps. Here, we explore and demonstrate that such anomalous enhancement concept may be extended to the emission mechanism. The finding makes the application of this concept even more exciting since it is feasible for both photon absorption and emission processes. Since the Fano generation in our proposed metamolecule only depends on its geometry, it is applicable to arbitrary host materials for emitting molecule, *e.g.* Poly(methyl methacrylate) (PMMA) and GaN. This emission enhancement concept is verified, interpreted and discussed in the following.

2. Modeling methods

A number of analytical and numerical methods have been successfully employed to model composed systems of emitting molecules and nanostructures including the Mie theory [43–46], Green's tensor method [47], the method-of-moment surface integral equation [48], the finite difference time domain method [49], the finite element method [23,50], the boundary element method (BEM) [51,52], the finite integration technique (FIT) [53], etc. In this work, all numerical calculations were carried out using the BEM method which is adapted to solve the full-wave Maxwell's equations as implemented in the MNPBEM toolbox [54]. The constituent nanoparticles of the proposed metamolecule are assumed to be silver (Ag) spheres. The refractive index of the host material is 1.4, corresponding to usual background materials, *e.g.* PMMA. The amount of vertices used to describe the spherical nanoparticle is 400 for all BEM calculations. The Ag permittivity with realistic material losses was interpolated from experimental data [55]. The emitting molecule is assumed to be a radiative dipole. Quantum effects [56–59] associated with non-local screening and tunneling of electrons between two neighboring nanoparticles with sub-nanometer inter-particle gaps are neglected.

3. Results and discussions

In order to outline the relevance of the proposed metamolecule for the enhanced light emission, we consider and compare several relevant composed metamolecule-single emitter systems, as shown in the insets of Fig. 1. In the first example, we consider a system consisting of single emitter and single Ag nanoparticle. The emitter is placed at a distance away from the particle surface of 10 nm. The enhanced emission measured by the Purcell factor is about 6 times over the system without the particle inclusion as shown in Fig. 1. The Purcell enhancement factor is defined as a ratio of the radiative decay rates of the systems with and without an inclusion of metal nanoparticles. The enhancement is attributed to the overlap of the LSPR of nanoparticle with the emission wavelength at around 390 nm. This is consistent with previous works in literature [60]. This enhancement factor can be strongly amplified at distances shorter than 10 nm due to near-field

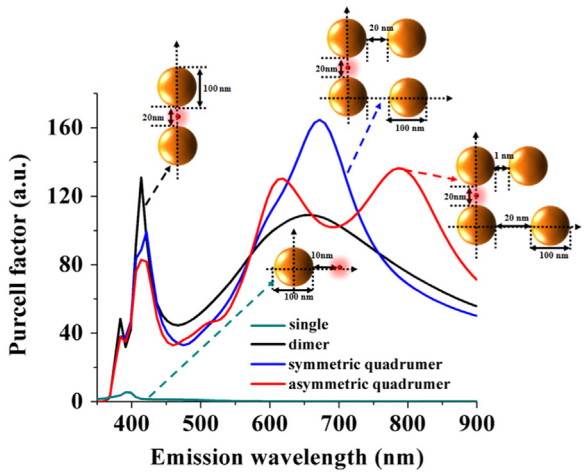

Fig. 1. Purcell enhancement factor as a function of emission wavelength of a dipole emitter located at $d_r = 10$ nm away from the metal surface in various plasmonic metamolecules (quadrumers) indicated in the panel.

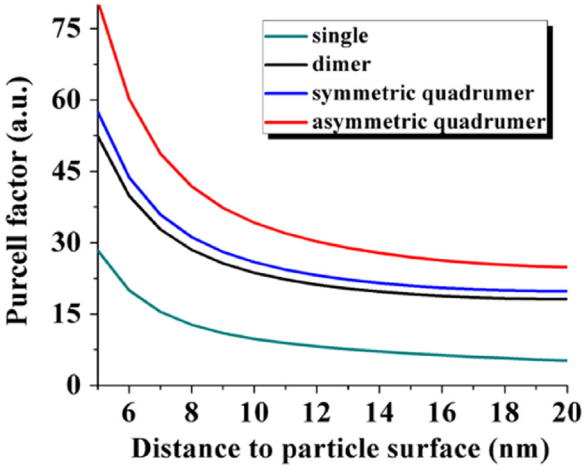

Fig. 2. Purcell enhancement factor of a dipole emitter as a function of emitter position in various plasmonic metamolecules (quadrumers).

enhancement caused by the plasmonic particle, even if the emission frequency is not perfectly matched with the particle's LSPR as seen in Fig. 2. However, at certain ultra-small distances the quenching of the emission may happen which decreases the radiative efficiency. To avoid the quenching effects, we only consider placing the emitter far away from the particle at a distance $d_r > 5$ nm. In order to increase the enhanced Purcell factor while keeping the emitter–particle separation $d_r > 5$ nm, proper positioning of the emitter inside the gap between two nanoparticle dimers was previously introduced [23]. Indeed, the enhancement factor can be achieved up to 130 times at the emission wavelength around 410 nm, corresponding to the dipolar frequency of the plasmonic dimer. In addition, the enhancement is observed over a broad band of frequencies due to near-field enhancement corresponding to the higher-order dipolar resonances of the dimer embedded in the dielectric environment as seen in Fig. 1. The broad scattering cross-section (SCS) of the dimer in the dielectric background corresponds to the broad emission enhancement as seen in Fig. 3. At certain distances between the emitter and the particle surface the emission enhancement caused by the dimer is higher than those caused by the single particle as also seen in Fig. 2. It is attributed to the strong coupling of two neighboring nanoparticles with ultra-small inter-particle gaps.

The Purcell factor can even be further enhanced when the emitter is suitably placed in a cluster of four symmetric