# Electromagnetic model for the loss compensation and emission properties of a dye-coated core-shell nanoparticle

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**Abstract**

We present a detailed electromagnetic model of the plasmonic response of a metal core-dielectric shell metallic nanoparticle covered with optically active dipoles (fluorescent molecules or quantum dots). We establish a complete description of the optical response based on Green's functions, which allows us to investigate high molecular coverages of the nanoparticle with either regular or random distribution of dye molecules, taking into account not only the interactions between nanoparticle (treated in a multipolar approach) and dye dipoles, but also between dyes molecules, either directly or via the nanoparticle. Our model shows a strong amplification and increase of quality of the plasmonic resonance, and provides a simple framework to explain the appearance of very sharp, "nanolaser"-type emissive states, based on an analysis of the collective optical modes of the dye-nanoparticle system.

## 1. Introduction

The high level of losses in metamaterials based on metallic nanostructures at optical frequencies is one of the most crucial issues for practical applications. One solution actively explored in the community is the coupling of externally pumped gain elements in the hope to compensate losses and amplify the desired response [1]. For a high enough level of gain, spasing and/or lasing can occur [2]. In this abstract, we present the first detailed electromagnetic model predicting the optical response of a plasmonic nanoparticle coated by a monolayer of dipolar emitters (representing dye molecules or quantum dots), in a geometry very similar to the experimental work of Noginov *et al.* [3].

## 2. Electromagnetic model

We consider an aggregate made of a single metal core-dielectric shell nanoparticle (NP) (core radius R, thickness shell $h$), on top of which a layer of $N$ fluorescent dyes is located at positions $\mathbf{r}_j$, with $j = 1, 2, ..N$ (we set origin $\mathbf{r} = \mathbf{0}$ at NP center) [see Fig. 1-(a)]. The aggregate is illuminated by an incident plane wave with field $\mathbf{E}^{\text{inc}}$. We assume that the aggregate has spherical symmetry, with a uniform (regular or statistical) distribution of dye molecules around the nanosphere. We want to represent the aggregate in terms of its total equivalent polarizability $\alpha^{\text{agg}}$, which relates the total aggregate dipole $\mathbf{p}^{\text{agg}}$ to the incident field $\mathbf{E}^{\text{inc}}$ as $\mathbf{p}^{\text{agg}} = \alpha^{\text{agg}}\mathbf{E}^{\text{inc}}(\mathbf{r} = \mathbf{0})$.

The induced dipole of each $j$th molecule can be found from the closed system $\mathbf{p}_j = \alpha_{\text{d}}\mathbf{E}_{\text{NP}}(r_j) + \frac{4\pi\omega^2}{c^2}\,\alpha_{\text{d}} \sum_{k=1}^{N} \underline{\mathbf{G}}(\mathbf{r}_j, \mathbf{r}_k)\mathbf{p}_k$, where $\omega$ is angular frequency, $c$ velocity of light, and $\mathbf{E}_{\text{NP}}(\mathbf{r})$ is the field scattered by the nanosphere in absence of the $N$ molecules, produced by the incident field $\mathbf{E}^{\text{inc}}$, plus the incident field itself. This system accounts for all molecule-nanoparticle interactions (multipolar) as well as molecule-molecule interactions, both directly and cooperatively mediated by the nanoparticle, with $\underline{\mathbf{G}}$ the dyadic Green's function (GF), representing the electric field at $\mathbf{r}_j$ due to an electric dipole at $\mathbf{r}_k$. It

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also involves the dye molecular polarizability, which is assumed radial to the NP surface and identical for all molecules, with magnitude $\alpha_{\rm d}$. The dyes are assumed to be pumped by an external pump field, and their response is simply modeled as a Lorentzian spectral line $\alpha^{\rm d} = (\mu\Delta Q)/[(\omega_{\rm em} - \omega) + i\gamma_{\rm em}]$, with $\omega_{\rm em}$ the central emission frequency, $\gamma_{\rm em}$ the collective damping accounting for multiple molecular transitions, $\Delta Q$ the molecular population inversion, and $\mu$ a coupling strength.

Our calculations show that, using the Dirac bra-ket notation, the expression for the overall polarizability of the aggregate is finally given as

$$\alpha^{\rm agg}(\omega) = \alpha^{\rm NP}(\omega) + \frac{\mu\Delta Q}{|\mathbf{E}^{\rm inc}(\mathbf{0})|^2} \times \sum_{n=1}^{N} \frac{\left\langle q_n | E^{\rm NP} \right\rangle \left\langle E^{\rm NP} | q_n \right\rangle}{(\omega_{em} - \omega - \Delta\omega_n) + i(\gamma_{em} - \Delta\gamma_n)} \tag{1}$$

In this notation, $\left|E^{\rm NP}\right\rangle$ is the $N$-dimensional vector representing the radial electric field at the $N$ dye positions, and $|q_n\rangle$ and $\Lambda_n = \Lambda_n' + i\Lambda_n''$ are respectively the eigenvectors and eigenvalues of the $N \times N$ Green function matrix made with elements $G_{jk} = \hat{\mathbf{r}}_j \underline{\mathbf{G}}(\mathbf{r}_j, \mathbf{r}_k)\hat{\mathbf{r}}_k$, where hats denote unit vectors. These $G_{jk}$ elements have been calculated in the near-field approximation and can be found analytically [4]. Finally, we used $\Delta\omega_n = \mu\Delta Q \times \Lambda_n'$ and $\Delta\gamma_n = \mu\Delta Q \times \Lambda_n''$, and $\alpha_{\rm NP}$ is the polarizability of the bare NP (without dyes).

Equation (1) reveals that the optical response of the aggregate is given as a sum over collective modes of the (NP plus dyes) system. The collective modes have individual central frequencies $\omega_n^{\rm res} = \omega_{\rm em} - \Delta\omega_n$ and spectral width $\gamma_{\rm em} - \Delta\gamma_n$. Whenever one given mode is in a situation such that $\gamma_{\rm em} \simeq \Delta\gamma_n$, it will resonate around its central frequency $\omega_n^{\rm res}$ with a strong amplitude, hence dominating the global response of the aggregate. Equivalently, this sharp resonance condition for mode $n$ can be written as

$$\Lambda_n'' = \frac{2\pi}{3} \frac{\omega_{\rm em}}{c\,\sigma_{\rm em}} \tag{2}$$

where the left hand-side depends on the nanoparticle geometry, constituent materials, number of dyes, while the right-hand side depends on the nature of the dye only, and is directly related to the dye peak emission cross-section $\sigma_{\rm em}$. When this condition is fulfilled, the losses for that mode will vanish and its spectral features will become close to singular: losses for this mode are "compensated" (or "mitigated"), and the global aggregate response will consequently display a very narrow peak.

## 3. Numerical results

We present results for aggregates composed of a gold core ($R = 35\,$nm), wrapped in a silica shell of variable thickness $h$, covered on the outside with $N = 1000$ randomly distributed dye molecules. The whole ensemble is immersed in water. For the dye, we consider $\sigma_{\rm em} = 0.26\,\text{nm}^2$ and emission wavelength $\lambda_{\rm em} = 2\pi c/\omega_{\rm em} = 520\,$nm. We take 10 multipoles into account in our calculations.

In Figs. 1 (b) and (d) the optical response of the aggregate is plotted, for two values of the silica shell thickness. In both cases, due to the coupling with the dyes, the aggregate's plasmon is strongly enhanced as compared to the bare plasmon for the NP and exhibits a situation where the loss compensation by coupling with gain is almost complete for some mode, resulting in a very sharp, intense spectral response. In Fig. 1 (b), one clearly sees that $\mathrm{Im}(\alpha^{\rm agg})$ is strongly negative in a very narrow spectral band, meaning that the system is acting like a net emitter of light within this band: our model is therefore a good candidate providing a simple description of the phenomenon of nanolasing/spasing seen experimentally in similar geometries [3].

We note that as $h$ is increased from 3 to 6 nm [Fig. 1 (b) and (d)], the amplitude of plasmon still increases, showing the crucial influence of the silica shell thickness. Indeed, if the thickness is increased further, the amplitude of the response will start diminishing, demonstrating that there is an optimal $h$. This piece of information is very relevant for chemists to guide synthesis. Finally, we observe on both figures that the resonant lineshapes are skewed and asymmetric: this is the signature of Fano resonances which take

 

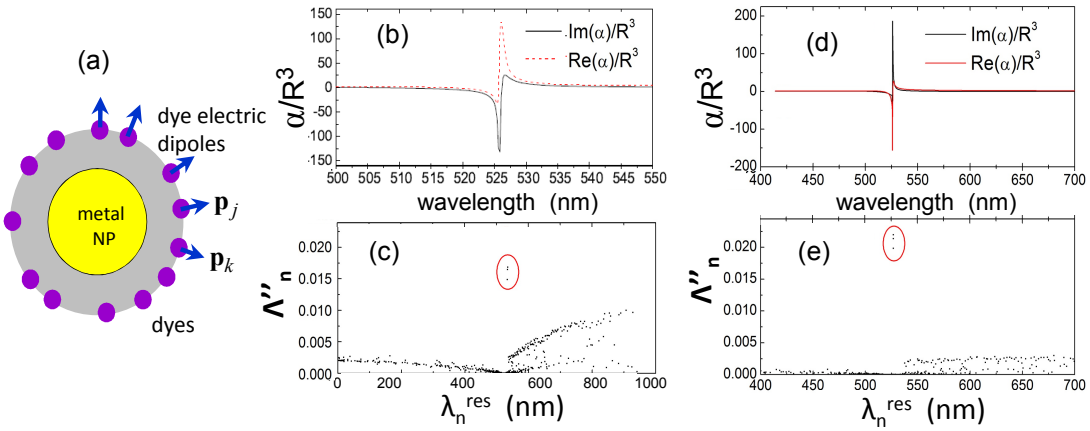


Fig. 1: (a) Core-shell nanoparticle covered with a layer of dye molecules; (b) and (d) Aggregate polarizability $\alpha_{\rm agg}$ (normalized by $R^3$) vs. wavelength, for a shell thickness $h = 3$ and 6 nm, respectively; (c) and (d) Corresponding distribution of the aggregate eigenmodes, for the same shell thicknesses $h = 3$ and 6 nm, respectively.

place through the interference of the (wide) gain dye resonance and the (sharp) resonance of the loss-compensated mode (see Ref. [5] where this point was studied in detail in a similar system, albeit with a different approach).

Figures 1 (c) and (e) provide some insight by showing the spectral distribution of the eigenmodes (collective modes) for the situations just discussed. Each point marked in these plots represents one eigenmode: the abscissa is the central wavelength of the eigenmode $\lambda_n^{\rm res} = 2\pi c/\omega_n^{\rm res}$, and the ordinate is given by $\Lambda_n''$, the imaginary part of the mode's eigenvalue calculated at $\omega = \omega_n^{\rm res}$. Our calculations show that the modes are always distributed in two sets (in accord with [4]): one set of three, isolated so-called "super-radiant" (bright) modes with high $\Lambda_n''$ (marked by a red oval) and a set of many "sub-radiant" (dark) modes with low $\Lambda_n''$. According to Eq. (2), modes with highest $\Lambda_n''$ are most easily loss-compensated (requiring much lower $\sigma_{\rm em}$), so that in practice, only super-radiant modes can be compensated; in addition, the bright nature of these modes explains why the aggregate emits light in the far-field ("nano-lasing").

As a last remark, it is extremely interesting to note that these super-radiant modes are always centered on the dye emission wavelength; this means that a loss-compensated aggregate will emit light at the dye frequency, *not* at the plasmon frequency. Numerical results with various dyes (not shown) confirm this; this finding supports the scenario of nanolasing as a plasmon-enhanced collective *dye* emission, and not a dye-enhanced *plasmon* emission. We also find, as could be expected, that the coupling between dyes and plasmon, and therefore loss compensation, is more efficient when the dye emission frequency is close to that of the plasmon.

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