INTERMOLECULAR RESONANCE ENERGY TRANSFER IN THE PRESENCE OF METALLIC NANOPARTICLES: FINITE ELEMENT SIMULATIONS

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Abstract: Plasmon resonances in metallic nanoparticles augment the Förster resonance energy transfer (FRET) between two molecules. We calculate and analyze comparatively the enhancement factors of FRET for a metallic nanosphere and for a metallic spherical nanoshell by finite element method (FEM). These calculations are compared with analytical results obtained from the knowledge of spectral properties of the Neumann-Poincaré (electrostatic) operator for sphere. With respect to the plain metallic nanosphere, the spherical nanoshell shows a greater tunability of energy range for which the energy transfer is enhanced. Our work can be relevant for using FRET for various applications regarding porous materials.

Key-words: Plasmonics; boundary integral equation method; Neumann-Poincaré (electrostatic) operator; finite element method; Förster resonance energy transfer.

1. INTRODUCTION

The resonance energy transfer between two molecules (a donor and an acceptor) is important in many photophysical and photochemical processes like photosynthesis and fluorescence probing [1, 2]. The mechanism of resonance energy transfer depends mostly on the distance between the donor (D) and acceptor (A). For distances within nanometer range the mechanism is quantum depending on the orbital overlap between D and A [2, 3]. On the other hand, for distances between 2 and approximately 10 nm, the mechanism is non-radiative governed by the electrostatic dipole–dipole interaction, the so called Forster resonance energy transfer (FRET) mechanism [1,2]. FRET depends on the inverse of the sixth power of the separation distance, hence it is rather weak. The enhancement of FRET can be obtained for instance by plasmonic effects due to the strong coupling between electromagnetic fields and collective oscillations in metals and in metallic nanoparticles [4, 5]. In our laboratory, a few carbon based porous materials have been synthesized and studied for concrete applications [6-8]. On the other hand, FRET can be used in different contexts regarding porous and porous-like materials [9-11]. Our work, studying FRET in the presence of a metallic nanoparticle, will shed more light on using FRET in more complex environments like those provided by porous materials.

Recently we have calculated analytically the enhancement factor due to a metallic nanosphere either by using directly the spectral properties of the Neumann-Poincaré (electrostatic) operator [12] or by building the Green's function [13] of the system [14]. The Neumann-Poincaré (electrostatic) operator is a useful tool for such problems [15-18], which can have analytical solutions for certain geometries [19]. In the present work we use a general numerical tool provided by finite element method (FEM) implemented in the multiphysics software COMSOL. Although FEM can be used in more complex geometries and systems, we study comparatively a metallic nanosphere and a metallic spherical nanoshell to understand the electrostatics behind FRET enhancement. In addition, some of our numerical examples are checked against analytical results.

2. FRET IN THE PRESENCE OF METALLIC SPHERICAL NANOPARTICLE AND SPHERICAL NANOSHELL

In FRET the molecules (D and A) are point-like dipoles, $\boldsymbol{d}_D$ and $\boldsymbol{d}_A$. The energy transfer between D and A is governed by the dipole-dipole interaction [1,2]. The enhancement factor of FRET due to a metallic nanoparticle is [5,20]

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$$A = \left| 1 + \frac{U_{ADind}}{U_{AD}} \right|^2 . \tag{1}$$

where $U_{AD} = -\boldsymbol{d}_A \cdot \boldsymbol{E}_{AD} = \boldsymbol{d}_A \cdot \nabla \Phi_D(\boldsymbol{r}_A)$ and $U_{ADind} = -\boldsymbol{d}_A \cdot \boldsymbol{E}_{ADind} = \boldsymbol{d}_A \cdot \nabla \Phi_{Dind}(\boldsymbol{r}_A)$ with $\Phi_D(\boldsymbol{r}_A)$ the electric potential induced by the donor at the acceptor site and $\Phi_{Dind}(\boldsymbol{r}_A)$ is the electric field induced by the nanoparticle at the acceptor site due to the donor dipole.

The energy transfer between a donor molecule (D) and an acceptor molecule (A) is studied in the vicinity of a spherical metallic nanoparticle (nanosphere) and of a spherical nanoshell. The nanosphere is as a sphere with radius of 25 nm, made of silver with dielectric function described by the Drude model with the following parameters: $\varepsilon_{infinity}=5$, $\omega_p=9.5$ eV, and $\delta=0.15$ eV. The donor molecule is modeled as a point-like dipole radially oriented with respect to the sphere and placed at a distance of 30 nm from the center of coordinates, or 5 nm from the nanoparticle's surface. The acceptor molecule is symmetrically placed in respect to the center of nanoparticle.

The spherical nanoshell is modeled as two concentric spheres with radii of 20 nm and 25 nm, having a dielectric core and metallic shell. The core of the nano-particle is made by hematite ($\varepsilon_{core}=9.5$) covered by a silver shell. The dielectric function of Ag layer is described by the Drude model with the parameters mentioned above. The donor and the acceptor molecules are placed at the same position as above, namely radially oriented with respect to the sphere and placed 5 nm above and below the nanoshell outer surface, respectively.

The numerical simulations were performed by using the AC/DC electrostatic solver, in frequency domain, of COMSOL Multiphysics software. The mesh structure is shown in Fig. 1.
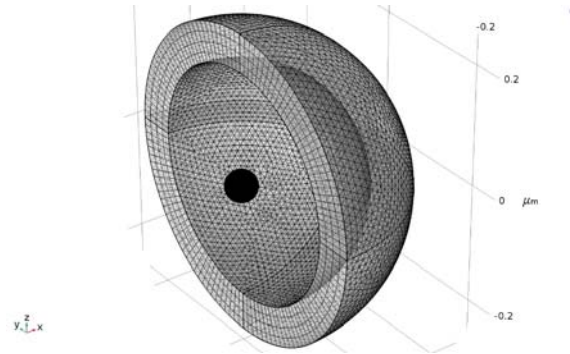

Fig.1. The meshed model including the nanoparticle and the spherical envelope with infinite elements shell (COMSOL).
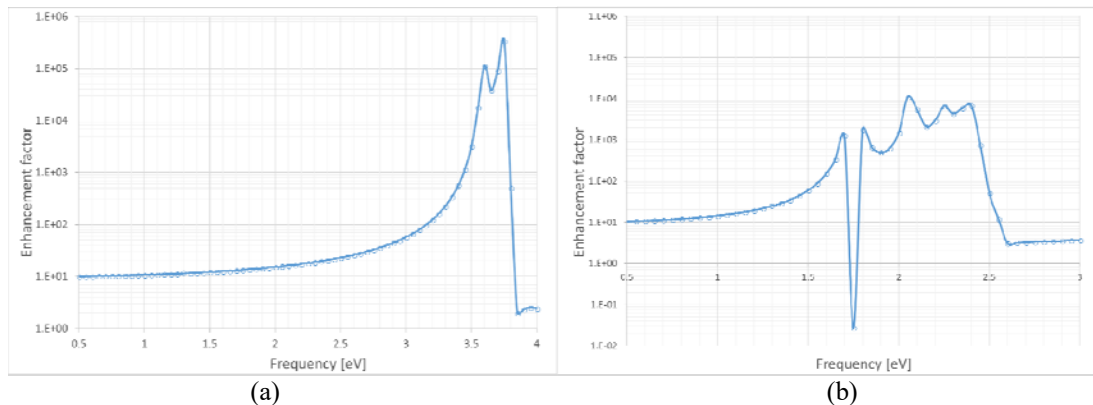

(a)	(b)

Fig.2. Numerically simulated enhancement factor A (log scale) as function of frequency for metallic nanosphere (a) and for metallic nanoshell (b).

In order to compute the enhancement factor of FRET, two numerical solutions were computed. First, solution *Sol1* include the electric field generated by the donor dipole and the field induced by the nanosphere or the nanoshell, $\boldsymbol{E}_{AD}+\boldsymbol{E}_{AD,ind}$. Second, the solution *Sol2* is computed without the nanosphere or the nanoshell in the configuration, and $\boldsymbol{E}_{AD}$ is evaluated. The computed enhancement factors as function of frequency (in eV) are represented in Fig. 2 for both the nanosphere and the nanoshell. Numerical results for nanosphere match very

well with analytical results found out earlier by us [12, 14]. We have found out maximum values of the enhancement factors of 3.35x10⁵ at 3.75 eV for nanosphere (Fig. 2a) and of 1.1x10⁴ at 2.05 eV for nanoshell (Fig. 2b). *Even though the maximum enhancement of FRET is greater for nanosphere the frequency window of enhancement is much larger and is placed at lower frequencies for nanoshell.* This behavior can be explained within the hybridization model of plasmon resonance [4]. In the hybridization picture, the plasmons formed on both metal-dielectrics interfaces of the nanoshell interact electrostatically, moving the bounding and anti-bounding plasmon resonances to lower and to higher frequencies, respectively. The frequency shift can be accordingly tuned by the thickness of the shell. On the other hand, it is known that the donor dipole excites all plasmon modes of the system [12, 14]. Moreover, the frequency shift is different for each plasmon mode, hence the nanoshell exhibits a larger window for enhancement.

To have a glimpse into the enhancement phenomenon we show the voltage (Fig. 3) and electric field (Fig. 4) distributions at the resonance frequencies of 3.75 eV for nanosphere and of 2.05 eV for nanoshell. From Figs. 3 and 4, we notice that at resonance there is a large image dipole created by the donor on the opposite side of both nanosphere and nanoshell. This image dipole is responsible for the enhancement of FRET.
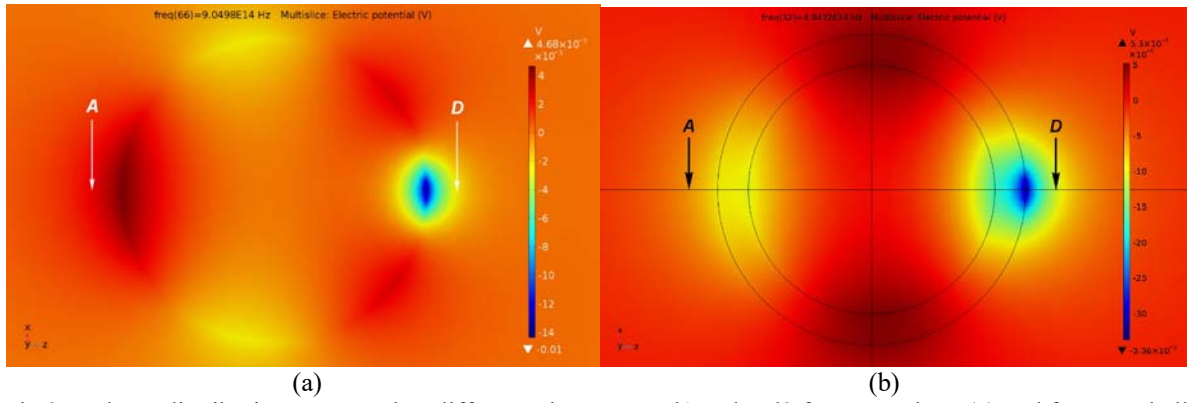

| (a) | (b) |

Fig.3. Voltage distribution computed as difference between Sol1 and Sol2 for nanosphere (a) and for nanoshell (b). This particular distribution corresponds to the maximum enhancement factor, located at 3.75 eV for nanosphere and at 2.05 eV for nanoshell.
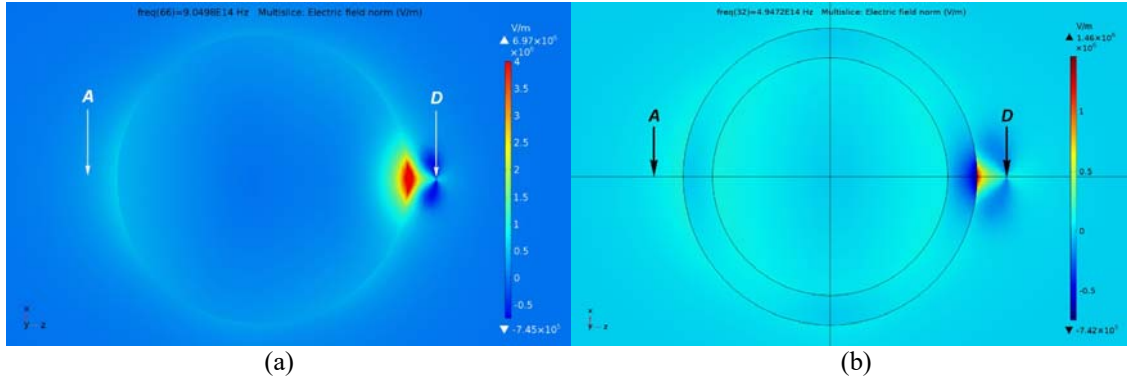

| (a) | (b) |

Fig.4. Electric field computed as difference between Sol1 and Sol2 for nanosphere (a) and for nanoshell (b). This particular distribution corresponds to the maximum enhancement factor, located at 3.75 eV for nanosphere and at 2.05 eV for nanoshell.

4. CONCLUSIONS

In this work, by finite element method (FEM), we calculated and analyzed comparatively the enhancement factors of Förster resonance energy transfer (FRET) due to a metallic nanosphere and a metallic spherical nanoshell. To check the validity of our FEM results, FEM calculations are compared with analytical results obtained from the knowledge of spectral properties of the Neumann-Poincaré (electrostatic) operator for sphere. We have found out that the maximum enhancement of FRET is greater for nanosphere, but the frequency window of FRET enhancement is much larger and is also placed at lower frequencies for nanoshell. Our numerical results can be qualitatively explained wit the hybridization model of plasmon resonance. For both the

nanosphere and the nanoshell the enhancement of FRET is due to the creation of a large image dipole on the opposite side of donor. Consequently, the spherical nanoshell shows a greater tunability of energy range for which the energy transfer is enhanced.

Acknowledgements

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