Gain assisted and gain functionalized core-shell nanoparticles: a multi-pronged approach to compensate loss in metamaterials

A. De Luca[1], M. Infusino[1], I. Pastoriza-Santos[2], M. Grzelczak[2], L. Curri[3], M. Striccoli[3] and G. Strangi[1]

[1]CNR-IPCF Licryl UOS Cosenza - Department of Physics, University of Calabria, 87036 Rende, Ponte P. Bucci - Cubo 31C (Italy) email: antonio.deluca@fis.unical.it
[2]Departamento de Quimica Fisica, Universidade de Vigo, 36310 Vigo, (Spain)
[3]CNR-IPCF UOS Bari, c/o Department of Chemistry, University of Bari, 70126 Bari, (Italy)

Abstract

Optical losses in meta-structures based on metal subunits represents a central topic towards the fabrication of metamaterials in the visible range, since most of the extra-ordinary electromagnetic properties expected in these structured systems are shadowed by unavoidable absorptive effects. In this paper we report experimental studies aimed to demonstrate effective chemical and physical approaches to mitigate the radiation damping effect by means of ”gain assisted” and ”gain functionalized” core-shell metal nanospheres selected as metamaterial building blocks. A multiscale strategy has been utilized to compare these two systems, showing that in both cases partial loss compensation can be obtained.

1. Introduction

The study of optical losses in plasmonic systems consisting of noble metal nanoparticles assembly represents a rapidly growing cutting edge research field towards the fabrication of low-loss meta-structures in the visible range. In fact, it is well known that most of the extra-ordinary electromagnetic properties expected in these systems are shadowed by unavoidable absorptive effects. Recently, theoretical studies have showed that bringing gain in proximity to metal subunits can reduce the strong radiation damping, in terms of reduction of imaginary part of the dielectric permittivity [1]. Thus enabling promising new applications of these materials in fields such as materials science [2], biophysics [3], molecular electronics, and fluorescence-spectral engineering based on surface-enhancement effects [4]. By compensating the strong losses caused by metal absorption would permit to operate at optical frequencies, enabling the possibility to investigate phenomena such as perfect lenses [5], cloaking [6, 7] and most not yet conceived. A recent experimental work performed on plasmonic structures with gain units dissolved in solution [8], showed that the presence of fluorescent molecules in a mixture may modify the scattering intensity as a function of the gain owing to the enhancement of the quality factor of surface plasmon resonances (SPRs). It is well known that relevant modifications of dye fluorescence placed in close proximity of metal NPs are due to mutual interactions with nanoparticle surface plasmons (SPs), including resonant energy transfer [9, 10, 11]. In 1989, Sudarkin and Demkovich [12] suggested to increase the propagation length of a surface-plasmon polariton (SPP, that is a surface electromagnetic wave propagating parallel to the metal/dielectric interface, possessing permittivities with opposite signs) by utilizing the population inversion created in the dielectric medium adjacent to the metallic film. The enhancement of the SPP (of the order of 10^5 to 10^4) at the interface between silver film and the dielectric medium

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with optical gain (laser dye) has been recently demonstrated in [13], and described by Noginov for Ag aggregates in ethanol solution [8]. Furthermore a relevant phenomenon of SP amplification by stimulated emission of radiation (SPASER), based on Förster-like energy transfer from excited molecules to resonating metallic nanostructures introduced by Stockman et al. [14, 15] in 2003, has been theoretically analyzed by Zheludev et al. [16] and experimentally demonstrated in Ref. [17]. At the same time, theoretical self-consistent calculation on gain assisted metamaterials was proposed in 2009 by Fang et al. [1], showing that 2D dispersive metamaterial losses can be compensated ($Im(\varepsilon) = 0$), whereas both positive and negative value of $Re(\varepsilon)$ can be obtained.

2. Experimental investigation

Here, we report experimental studies aimed to demonstrate effective chemical and physical approaches to mitigate the radiation damping effect by means either "gain assisted" and "gain functionalized" core-shell metal nanospheres selected as metamaterial building blocks. The main goal into these two approaches consists of including fluorescent guest molecules in the designed nanostructure by interlocking them with the plasmonic nanoparticles (gain assisted) or by introducing them (quantum dots or organic dyes) right at the heart of the engineered nanoparticle (gain functionalized). A multi-pronged synthetic strategy has been followed to bring required functionalities at the plasmonic NPs acting as lowloss nano-resonators. As first step organic dyes have been dissolved in solution, to optimize compatibility, spectral overlapping and non-radiative transfer rate, then the selected fluorescent molecules have been encapsulated within the shell of noble metal NPs. In particular, gain functionalized metal nanoparticles consist of a gold core (diameter d 60 nm) coated with a silica shell (30 nm thick) containing organic dye molecules. Photostable organic dye [Rhodamine 6G (R6G)] was optically excited by means of laser pulses at 355nm, showing that its gain curve overlaps the plasmon band of gold NPs in both systems: "gain assisted" (system a) and "gain functionalized" (system b) (see Fig. 1). The fluorescence quenching observed in

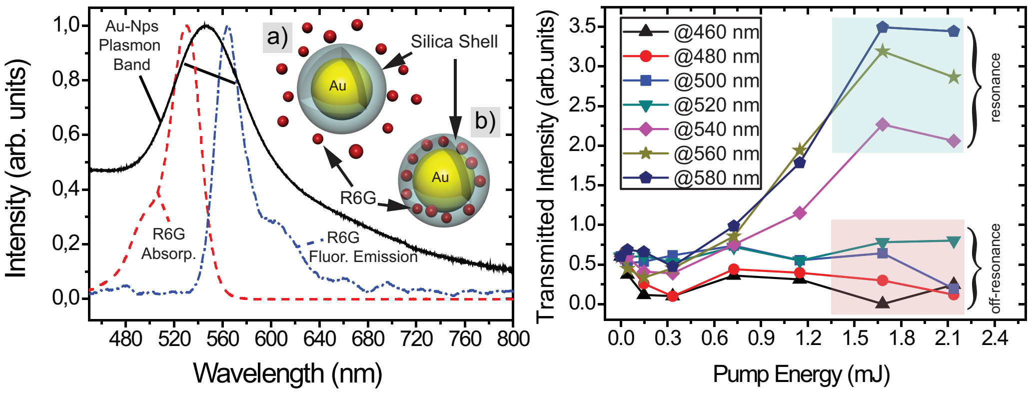

Fig. 1: Absorption and emission spectrum of R6G dye in ethanol and plasmon bands of gain "assisted" and gain "functionalized" gold nanoparticles. a) Sketch of the gain assisted system in which R6G dye molecules have been dissolved in the ethanol solution of gold core/silica shell NPs; b) R6G has been encapsulated in the silica shell. c) Transmission enhancement of a probe beam (broadband) was observed only for wavelengths inside the resonance band

system (a) with respect to the pure R6G ethanol based solution (same concentration), when optically pumped with large spotted pulse trains of a tripled Nd:Yag laser ($\lambda = 355nm$) at the same pump energy, can be considered the consequence of resonant nonradiative energy transfer process occurring from gain molecules to metal units present in the surrounding volume, that causes the lowering of the radiative rate. At the same time, time-resolved fluorescence spectroscopy along with pump-probe experiments have been performed either on gain assisted and gain functionalized systems, in order to obtain a comparative analysis of gain induced optical loss modifications. In fact, according to Beer-Lambert-Bouguer law, by

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measuring simultaneously Rayleigh scattering and transmission, either in absence or in presence of gain, allow to understand if the absorptive power of the material is affected by excitation energy transfer. Thus, modifications of Rayleigh scattering and transmitted intensity of a constant probe beam ($\lambda = 532nm$ or broadband (see Fig.1c)) have been monitored as a function of the pump energy for both systems (excitation @ 355 nm).

3. Conclusions

In conclusion, bringing gain to strongly absorptive meta-subunits can reduce the radiation damping, either by gain assisted nanoparticles through proper incorporation of gain molecules in solution and by functionalizing the single nanoparticle with gain units. Thus, demonstrating the capabilities to fabricate metamaterials where gain media can be adequately inserted at different scale levels ranging from nanoscale to the macroscopic scale. Therefore, these results are of particular importance to move metamaterials from fundamental scientific challenges to applied materials.

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