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Complex modes and near-zero permittivity in 3D arrays of plasmonic nanoshells: loss compensation using gain [Invited]

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Abstract: We report on the possibility of adopting active gain materials (specifically, made of fluorescent dyes) to mitigate the losses in a 3D periodic array of dielectric-core metallic-shell nanospheres. We find the modes with complex wavenumber in the structure, and describe the composite material in terms of homogenized effective permittivity, comparing results from modal analysis and Maxwell Garnett theory. We then design two metamaterials in which the epsilon-near-zero frequency region overlaps with the emission band of the adopted gain media, and we show that metamaterials with effective parameters with low losses are feasible, thanks to the gain materials. Even though fluorescent dyes embedded in the nanoshells' dielectric cores are employed in this study, the formulation provided is general, and could account for the usage of other active materials, such as semiconductors and quantum dots.

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OCIS codes: (250.5403) Plasmonics; (160.3918) Metamaterials; (160.1245) Artificially engineered materials.

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1. Introduction

Metamaterials have been proposed for several innovative applications and have allowed, for example, the design of "perfect lenses" [1], and invisibility cloaks [2]. In general, however, plasmonic-based metamaterial losses at optical frequencies have been found to be significantly large, and thus have limited the application scenario. However, at infrared, ultraviolet and optical frequencies, the use of plasmonics mixed with active photonic materials has been found to be promising due to the fact that the gain experienced through the emission of a gain medium is capable of counteracting the high attenuation experienced by the electromagnetic wave due to the presence of the metal. This may indeed lead to loss-mitigated metamaterials, enabling effective permeability or low permittivity parameters at optical frequencies.

One of the key points is designing the metamaterial such that the frequency region of interest overlaps with the emission spectrum of the adopted gain medium. Different gain sources, optically pumped, could be adopted for this purpose: fluorescent dyes (e.g., Rhodamine, Fluorescein, Coumarin), semiconductor materials and quantum dots (e.g., InGaAs-GaAs quantum dots), rare earth materials (e.g., erbium).

It has been reported that the usage of the gain medium with metamaterials can provide a larger effective gain than when used alone, due to the strong local field enhancement inside the metamaterials [3,4].

Positive net gain (i.e., the gain is larger than the losses) has been shown to be possible over macroscopic distances in a dielectric-metal-dielectric plasmonic waveguide, where the gain has been provided by an optically pumped layer of fluorescent conjugated polymer (known to have very large emission cross sections) adjacent to the metal surface [5]. Also, a direct measurement of gain in propagating plasmons using the long-range surface plasmon-polariton supported by a symmetric metal strip waveguide that incorporates optically pumped dye molecules in solution as the gain medium has been shown [6]. Furthermore, optical loss compensation effects have been recently experimentally observed in [7], and [8], where Coumarin C500 and Rhodamine 6G fluorescent dyes were encapsulated into the dielectric shell of randomly dispersed nanoshell particles.

Effective parameters of metamaterials made of nanoshells with active gain materials embedded in the dielectric core, designed to operate in the visible range of the spectrum between 400 nm and 700 nm, have been simulated in [9] by artificially setting the imaginary part of the dielectric core to fixed ideal loss/gain conditions, i.e., realistic gain materials have not been considered. A detailed analysis observing the effects of the gain value in the nanoshells' core and of the density of the inclusions has been provided in [9] to investigate the tunability of such metamaterials. For 3D periodic arrays, the authors of [9] concluded that the effective permittivity can be engineered to assume both positive and negative values by selecting appropriately the lattice period and the gain value in the core of the nanoshells. In this paper we confirm the results found in [9], and moreover we show complex modes in the 3D lattice and utilize realistic parameters for the gain medium to analyze feasibility. Loss compensation of the intrinsic losses of metals at optical frequencies by using gain materials has also been proposed in [10–14]. In [15], it has been shown that metallic nanoparticles (nanoshells and nanorods) influence the properties of adjacent fluorophores; in that paper, the authors have shown an improvement in the quantum yield (defined here in Sec. 2.3) of the fluorophore IR800 showing the potential for contrast enhancement in fluorescence-based bioimaging. Similarly, in [16], Ruby dyes were incorporated into the dielectric core of

randomly dispersed nanoshell particles, and an emission enhancement has been observed with respect to the case in absence of the metallic shell.

A computational approach including rate equations has been presented in [17] and references therein, allowing for a self-consistent treatment of a split ring resonator (SRR) array with a gain layer underneath, showing numerically that the magnetic losses of the SRR can be compensated by the gain. Rate equations have also been used in [18]. A review regarding the management of loss and gain in metamaterials has been presented in [19], and references therein.

In this paper, we provide the analysis of a loss-compensated metamaterial at optical frequencies through optical pumping. In particular, we analyze a 3D periodic array of dielectric-core metallic-shell nanospheres, assuming fluorescent dyes encapsulated into the core of each spherical nanoparticle. Each nanoshell is modeled as a single electric dipole and by its polarizability, using the single dipole approximation (SDA) [20–22] and the metal permittivity is described by the Drude model. We compute the modes following the procedure described in [21,22]. Then, also by using Maxwell Garnett homogenization theory [23,24], we compute the relative effective permittivity ϵ_{eff} . Three interesting frequency regions can be outlined depending on its value: (i) one where ϵ_{eff} is rather large and positive; (ii) one where ϵ_{eff} is rather large and negative; and (iii) one where ϵ_{eff} is close to zero (either positive or negative), also called the epsilon-near-zero (ENZ) frequency region, which has been proposed as a viable way for a number of applications including cloaking, tunneling, high directivity radiators, optic nanocircuits, etc, as reported for example in [25] and references therein. Certainly, high losses hinder the interesting properties in such frequency regions, and loss mitigation mechanisms are inherently required to overcome this issue. In this paper, we are interested in showing a formulation for loss compensation and then specifically reducing losses in the ENZ frequency region. Therefore, we design metamaterials such that the effective ENZ region overlaps with the emission spectrum of the considered dyes, and we observe that loss-compensation is feasible. Notice however that the analysis here reported does not limit the usage of gain materials to overcome the losses in other frequency regions.

The structure of the paper is as follows. Mode analysis, Maxwell Garnett theory and modeling of the active gain material are introduced in Sec. 2. Then, in Sec. 3, we use two different fluorescent dyes (Rhodamine 6G and Rhodamine 800) to mitigate the losses for two particular metamaterials' designs. Conclusions are reported in Sec. 4.

Fig. 1. 3D periodic array of dielectric-core metallic-shell nanospheres embedded in a homogeneous medium with permittivity ϵ_h . The core radius is r_1 , with permittivity ϵ_1 ; the shell outer radius is r_2 , with permittivity ϵ_2 ; a , b and c are the periodicities along x -, y - and z -direction, respectively. (a) The shell is made of silver. (b) The shell is made of gold.

2. Simulation model

The structure under analysis is the 3D periodic array of dielectric-core metallic-shell nanospheres reported in Fig. 1. We analyze two cases, first shells made of silver in Fig. 1(a), and then shells made of gold in Fig. 1(b). According to the experimental results in [26], gold is more lossy than silver at optical frequencies: our purpose is then to show that we can design loss-compensated metamaterials by using fluorescent dyes. The monochromatic time harmonic convention, $\exp(-i\omega t)$, is assumed here and throughout the paper, and is therefore suppressed hereafter. Under this time harmonic dependence, a lossy material has $\text{Im}[\varepsilon] \geq 0$; a material able to provide gain, instead, has $\text{Im}[\varepsilon] < 0$ in the emitting frequency range (provided a suitable temporal dispersion satisfies the constraints dictated by causality, i.e., Kramers-Kronig relations have to be satisfied [27–30]). A totally loss-compensated metamaterial is a material that has an effective permittivity and/or permeability with null imaginary part. We describe modal analysis in Sec. 2.1, how to retrieve effective parameters in Sec. 2.2 and the gain material modeling in Sec. 2.3.

2.1 Modal analysis for periodic arrays of plasmonic nanoshells

We model each nanoshell as a single electric dipole at optical frequencies. As such, for a plasmonic spherical particle the induced electric dipole moment is

$$\mathbf{p} = \alpha_{\text{ee}} \mathbf{E}^{\text{loc}}, \quad (1)$$

where α_{ee} is the electric polarizability of the nanoshell, $\mathbf{E}^{\text{loc}}$ is the local field produced by all the nanoshells of the array except the considered nanoshell plus the external incident field to the array, and bold letters refer to vector quantities. According to the Clausius-Mossotti approximation, the electric polarizability of a nanoshell is [20,23,31,32]

$$\alpha_{\text{ee}}^{-1} = \frac{1}{4\pi\varepsilon_h\varepsilon_0r_2^3} \frac{(\varepsilon_2 + 2\varepsilon_h)(\varepsilon_1 + 2\varepsilon_2) + 2\beta(\varepsilon_2 - \varepsilon_h)(\varepsilon_1 - \varepsilon_2)}{(\varepsilon_2 - \varepsilon_h)(\varepsilon_1 + 2\varepsilon_2) + \beta(2\varepsilon_2 + \varepsilon_h)(\varepsilon_1 - \varepsilon_2)} - i \frac{k^3}{6\pi\varepsilon_h\varepsilon_0}, \quad (2)$$

where ε_h is the relative permittivity of the host medium (which can be vacuum, glass, water, or any other solvent), ε_0 is the absolute permittivity of free space, $k = \omega\sqrt{\varepsilon_h}/c_0 = k_0\sqrt{\varepsilon_h}$ is the host medium wavenumber, with k_0 denoting the free space wavenumber and c_0 the speed of light in free space, ε_1 is the relative permittivity of the core (with radius r_1), and ε_2 is the relative permittivity of the shell (with outer radius r_2). Furthermore, $\beta = \rho^3$, with $\rho = r_1/r_2$. The last imaginary term in Eq. (2) has been introduced to account for particle radiation [20,21]. According to Mie theory, instead, the polarizability of a nanoshell is [20]

$$\alpha_{\text{ee}} = \frac{6\pi i \varepsilon_h \varepsilon_0}{k^3} \frac{\psi_1(kr_2)A - m_2\psi_1'(kr_2)B}{\xi_1(kr_2)A - m_2\xi_1'(kr_2)B}, \quad A = \psi_1'(m_2kr_2) - C\chi_1'(m_2kr_2), \quad (3)$$

and

$$B = \psi_1(m_2kr_2) - C\chi_1(m_2kr_2), \quad C = \frac{m_2\psi_1(m_2kr_1)\psi_1'(m_1kr_1) - m_1\psi_1'(m_2kr_1)\psi_1(m_1kr_1)}{m_2\chi_1(m_2kr_1)\psi_1'(m_1kr_1) - m_1\chi_1'(m_2kr_1)\psi_1(m_1kr_1)}, \quad (4)$$

with $\psi_1(\rho) = \rho j_1(\rho) = \sin \rho / \rho - \cos \rho$, $\xi_1(\rho) = \rho h_1^{(1)}(\rho) = (-i/\rho - 1)e^{i\rho}$ and $\chi_1(\rho) = -\rho y_1(\rho) = \cos \rho / \rho + \sin \rho$ the Riccati-Bessel functions [33], and $m_1 = \sqrt{\varepsilon_1/\varepsilon_h}$,

$m_2 = \sqrt{\varepsilon_2 / \varepsilon_h}$ are the core and shell relative refractive indexes. Notice that a prime in Eqs. (3) and (4) refers to the first derivative of the function with respect to its argument.

In this paper we consider dielectric-core metallic-shell particles, with $\varepsilon_1 = \varepsilon_r$ and $\varepsilon_2 = \varepsilon_m$, where ε_r is the relative permittivity of the chosen dielectric material and the metal permittivity ε_m is described through the Drude model as

$$\varepsilon_m = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (5)$$

where ω_p is the plasma angular frequency, γ the damping term, and ε_∞ is a “high frequency” permittivity determined to match experimental data in the visible region.

Consider now a 3D periodic array of nanoshells, immersed in a homogeneous background, with relative permittivity ε_h , for which each nanoshell is placed at positions $\mathbf{r}_n = \mathbf{r}_0 + \mathbf{d}_n$, where $n \equiv n_1, n_2, n_3 = 0, \pm 1, \pm 2, \dots$, is a triple index, and $\mathbf{d}_n = n_1 a \hat{\mathbf{x}} + n_2 b \hat{\mathbf{y}} + n_3 c \hat{\mathbf{z}}$, $\mathbf{r}_0 = x_0 \hat{\mathbf{x}} + y_0 \hat{\mathbf{y}} + z_0 \hat{\mathbf{z}}$ (where a caret on top of a bold letter refers to unit vector quantities), and a , b and c are the periodicities along x -, y - and z -direction, respectively [21,22,34]. Suppose that the array is then excited by a plane wave or by a quasi-periodic excitation with wavevector $\mathbf{k}_B = k_x \hat{\mathbf{x}} + k_y \hat{\mathbf{y}} + k_z \hat{\mathbf{z}}$. The formulation here adopted has been described elsewhere [21,22,35]. Briefly, mode analysis in the 3D periodic array is performed by computing the eigensolutions of the homogeneous version of

$$\underline{\mathbf{A}}(\mathbf{k}_B) \cdot \mathbf{p}_0 = \alpha_{ee} \mathbf{E}^{\text{inc}}(\mathbf{r}_0), \quad \underline{\mathbf{A}}(\mathbf{k}_B) = \underline{\mathbf{I}} - \alpha_{ee} \underline{\tilde{\mathbf{G}}}^\infty(\mathbf{r}_0, \mathbf{r}_0, \mathbf{k}_B), \quad (6)$$

i.e., when no impressed excitation is present $\mathbf{E}^{\text{inc}}(\mathbf{r}_0) = \mathbf{0}$, and a bar under a bold letter refers to dyadic quantities. The term $\underline{\tilde{\mathbf{G}}}^\infty(\mathbf{r}_0, \mathbf{r}_0, \mathbf{k}_B)$ represents the regularized Green’s function [35], and provides the field contribution evaluated at $\mathbf{r}_0$ produced by all the nanoshells but the one at $\mathbf{r}_0$, and $\underline{\mathbf{I}}$ is the identity dyad. In other words, the complex mode wavenumbers $\mathbf{k}_B$ are computed by solving for the complex zeroes of the determinant of $\underline{\mathbf{A}}(\mathbf{k}_B)$. In the following, we assume that the modes travel along the z direction with wavenumber k_z (for the sake of brevity modes with oblique propagation direction are not considered in this feasibility study).

2.2 Effective parameters

In general, Maxwell Garnett theory [23,24] can be applied to retrieve the effective parameters of a composite medium as

$$\varepsilon_{\text{eff}} = \varepsilon_h + \frac{\varepsilon_h}{N_D^{-1} \left[\varepsilon_0 \varepsilon_h \alpha_{ee}^{-1} + i \frac{k^3}{6\pi} \right] - \frac{1}{3}}, \quad \mu_{\text{eff}} = 1 + \frac{1}{N_D^{-1} \left[\alpha_{mm}^{-1} + i \frac{k^3}{6\pi} \right] - \frac{1}{3}}, \quad (7)$$

where $N_D = f / V_N$, with f the filling fraction $f = V_N / V_L$ (assuming simple cubic lattices), V_N is the nanoshell volume and V_L is the unit cell volume, and α_{mm} is the magnetic polarizability of a nanoshell. Then, the effective refractive index can be calculated as $n_{\text{eff}} = \sqrt{\varepsilon_{\text{eff}} \mu_{\text{eff}}}$. Moreover, as we will do in the following, the effective refractive index is also computed by using mode analysis as

$$n_{\text{eff}} = \frac{k_z}{k_0}, \quad (8)$$

where k_z is the wavenumber of the “dominant” mode (assuming there is one) computed from mode analysis.

2.3 Modeling of the gain material

We assume to model the gain material made of fluorescent dye molecules as a four level atomic system [17,36,37], as also proposed in [38,39], with occupation density $N_i(\mathbf{r}, t)$ of the gain medium in the i -th state, $i = 0, 1, 2, 3$, with $N_0(\mathbf{r}) + N_1(\mathbf{r}) + N_2(\mathbf{r}) + N_3(\mathbf{r}) = \bar{N}_0$, where $\bar{N}_0$ is the total dye concentration, which corresponds to the $N_0(\mathbf{r})$ concentration in absence of pumping (i.e., $N_1(\mathbf{r}) = N_2(\mathbf{r}) = N_3(\mathbf{r}) = 0$, thus $N_0(\mathbf{r}) = \bar{N}_0$). Furthermore, τ_{ij} is the lifetime for the transition from state i to the lower state j , and Γ_{pump} is the pumping rate from level 0 to level 3. According to [36,37], locally, the polarization density at the emission frequency band $\mathbf{P}_e(\mathbf{r}, t)$ obeys to the semi-classical “equation of motion”

$$\frac{\partial^2}{\partial t^2} \mathbf{P}_e(\mathbf{r}, t) + \Delta \omega_a \frac{\partial}{\partial t} \mathbf{P}_e(\mathbf{r}, t) + \omega_a^2 \mathbf{P}_e(\mathbf{r}, t) = -\sigma_a \Delta N(\mathbf{r}, t) \mathbf{E}(\mathbf{r}, t), \quad (9)$$

where $\Delta \omega_a$ is the bandwidth of the dye transition at the emitting angular frequency ω_a , $\Delta N(\mathbf{r}, t) = N_2(\mathbf{r}, t) - N_1(\mathbf{r}, t)$ is the population inversion, and σ_a the coupling strength of $\mathbf{P}_e(\mathbf{r}, t)$ to the electric field $\mathbf{E}(\mathbf{r}, t)$. The expression of σ_a has been provided, for example, in [36] (pages 221-222, chapter 5) as $\sigma_a = 6\pi\epsilon_0 c_0^3 \gamma_{\text{rad}} / (\sqrt{\epsilon_r} \omega_a^2)$ (see also [40]), where γ_{rad} is the radiative transition rate from level 2 to level 1, whose value can be obtained from the quantum yield $\gamma_{\text{rad}} / (\gamma_{\text{rad}} + \gamma_{\text{non-rad}}) = \gamma_{\text{rad}} \tau_{21}$, obtained experimentally and readily available for the dyes later considered.

Assuming time harmonic polarization density and electric field $\mathbf{P}_e(\mathbf{r}, t) = \text{Re}[\mathbf{P}_e(\mathbf{r}) e^{-i\omega t}]$, $\mathbf{E}(\mathbf{r}, t) = \text{Re}[\mathbf{E}(\mathbf{r}) e^{-i\omega t}]$, and constant population inversion ΔN (i.e., steady state), Eq. (9) becomes

$$\mathbf{P}_e(\mathbf{r}) = \epsilon_0 \chi_e \mathbf{E}(\mathbf{r}), \quad \chi_e = \frac{1}{\epsilon_0} \frac{\sigma_a \Delta N}{\omega^2 + i\Delta \omega_a \omega - \omega_a^2}. \quad (10)$$

According to chapter 2 in [36], the total displacement might be written as

$$\mathbf{D}(\mathbf{r}) = \epsilon_0 \mathbf{E}(\mathbf{r}) + \mathbf{P}_r(\mathbf{r}) + \mathbf{P}_e(\mathbf{r}) = \epsilon_0 \epsilon_r \mathbf{E}(\mathbf{r}) + \mathbf{P}_e(\mathbf{r}), \quad (11)$$

where $\mathbf{P}_r(\mathbf{r})$ is the polarization contribution due to the dielectric medium hosting the gain material, and $\mathbf{P}_e(\mathbf{r})$ is the polarization contribution due to the dispersed gain material itself, from which the effective absolute permittivity of the gain medium is

$$\epsilon_g = \epsilon_0 \epsilon_r + \frac{\sigma_a \Delta N}{\omega^2 + i\Delta \omega_a \omega - \omega_a^2}. \quad (12)$$

The model shown in Eqs. (9)–(12) is detailed in standard laser textbooks (such as [36]). Here it has been just briefly summarized to guide the reader and to introduce every dye molecular

parameter that will be adopted in the following sections. One should notice that as mentioned in [36] (pages 104-105, chapter 2), $\mathbf{D}(\mathbf{r})$ and $\mathbf{P}_e(\mathbf{r})$ could be expressed in two slightly different ways; to avoid ambiguities and misunderstandings, we report in Eqs. (10) and (11) the expressions we used.

Under stationary regime assumption (constant electron densities in any state) with time harmonic polarization, the population inversion is

$$\Delta N = \frac{(\tau_{21} - \tau_{10})\Gamma_{\text{pump}}}{1 + (\tau_{32} + \tau_{21} + \tau_{10})\Gamma_{\text{pump}}} \bar{N}_0, \quad (13)$$

where we have assumed that the electric field is small enough to neglect nonlinear saturation terms (as also discussed in [41]) that may induce depletion of the population inversion [36]. The relation of Eq. (13) to the pump light intensity is not straightforward when the gain medium is enclosed by a nanoshell or close to other nano scatterers, whereas it is rather simple for an open gain medium. As a first approximation, one can consider the relation in open gain media where $\Gamma_{\text{pump}} = \sigma_{\text{abs}} I_{\text{pump}} / (hf_{30})$, where σ_{abs} is the absorption cross section, I_{pump} is the pump intensity, h is the Planck constant, and f_{30} is the pump frequency [36]. A further improvement of the model (which will be performed in a future study) is based on analyzing the electrodynamic system at the pump frequency and on determining local pump fields and thus local absorptions. From Eqs. (12) and (13) the linearized active constitutive permittivity of the gain material in the nanoparticle cores is

$$\epsilon_g = \epsilon_0 \epsilon_r + \frac{\sigma_a}{\omega^2 + i\Delta\omega_a \omega - \omega_a^2} \frac{(\tau_{21} - \tau_{10})\Gamma_{\text{pump}}}{1 + (\tau_{32} + \tau_{21} + \tau_{10})\Gamma_{\text{pump}}} \bar{N}_0. \quad (14)$$

3. Results of epsilon near zero composite materials with mitigated loss

Two cases are assumed, the first one made by silver shells (Fig. 1(a)), the second one made by gold shells (Fig. 1(b)), thus exhibiting resonance at lower frequency.

3.1 Case with silver shells

We assume that Rhodamine 6G (R6G) dye molecules are into the dielectric core as in Fig. 1(a). According to [42–45], R6G has the following parameters: center emission frequency $f_a = 526$ THz (570 nm) (an homogeneously broadened Lorentzian lineshape is assumed), wavelength linewidth is $\Delta\lambda_a = 30$ nm, and consequently $\Delta\omega_a = 2\pi\Delta\nu_a$, with frequency linewidth $\Delta\nu_a = c_0\Delta\lambda_a / \lambda_a^2 = 27.7$ THz. Assuming a four level system, the pumping wavelength (between level 0 and level 3) is 531 nm (565 THz), and the decay rate from level 2 to level 1 is $1/\tau_{21}$, where $\tau_{21} = 3.99$ ns. Moreover, the other decay rates from level 3 to level 2 and from level 1 to level 0 are $1/\tau_{32} = 1/\tau_{10}$, where $\tau_{32} = \tau_{10} = 100$ fs. Also, we consider two different densities of the dye molecules as $\bar{N}_0 = 3 \times 10^{18} \text{ cm}^{-3}$, and $\bar{N}_0 = 6 \times 10^{18} \text{ cm}^{-3}$ corresponding to about 5 mM and 10 mM, respectively. The coupling constant σ_a in Eq. (9) is evaluated as discussed in Sec. 2.3 (and also shown in chapter 5 in [36]), for which $\sigma_a = 6.55 \times 10^{-8} \text{ C}^2/\text{kg}$, having used $\gamma_{\text{rad}} = 2.38 \times 10^8 \text{ s}^{-1}$ as in [45] (assuming a quantum yield of 0.95, defined at the end of Sec. 2.3).

3.1.1 Mode analysis and effective parameters computation

In this section, we adopt the structure in Fig. 1(a). The outer shell radius is $r_2 = 25$ nm, the dielectric core and environment are made by a material with $\epsilon_r = \epsilon_h = 2.25$, $r_1 = 20$ nm ($\rho = r_1/r_2 = 0.8$), and $a = b = c = 75$ nm. The shell is made of silver, with relative permittivity $\epsilon_2 = \epsilon_m$, with ϵ_m as in Eq. (5), whose Drude model parameters are $\epsilon_\infty = 5$, $\omega_p = 1.37 \times 10^{16}$ rad/s and $\gamma = 27.3 \times 10^{12}$ s⁻¹ [46,47]. The core has a relative permittivity $\epsilon_1 = \epsilon_g / \epsilon_0$, with ϵ_g as in Eq. (14) with the parameters for R6G. We use the nanoshell Mie electric polarizability expression in Eq. (3) for the results in Fig. 2, where we show the modes in the 3D lattice, for transverse polarization, traveling along the z direction, for three cases: (i) accounting for metal losses, (ii) ideal lossless case (i.e., $\gamma = 0$ in Eq. (5)), and (iii) in presence of gain (10 mM of R6G optically pumped at 531 nm with pumping rate $\Gamma_{\text{pump}} = 1.5 \times 10^9$ s⁻¹).

Fig. 2. Wavenumber dispersion diagram versus frequency for T-pol for the structure in Fig. 1(a), using the polarizability in Eq. (3). (a) Real part and (b) imaginary part of the wavenumber $k_z = \beta_z + i\alpha_z$, for lossy, lossless and loss-compensated cases.

Fig. 3. (a) Real part and (b) imaginary part of the effective relative permittivity for the structure in Fig. 1(a) computed in three different ways: by Maxwell Garnett, by using the polarizability in (2) (MG – CM); the polarizability in Eq. (3) (MG – Mie); and mode analysis.

As stated in Sec. 2.2, by using Eq. (8), it is possible to compute the effective refractive index of the homogenized array from the wavenumber information reported in Fig. 2. Then, we observed by using Eq. (7) with the magnetic polarizability of a nanoshell that the effective

permeability $\mu_{\text{eff}} \approx 1$ for the entire frequency region analyzed (the maximum deviation from 1 is at 100 THz (3 μm), where $\mu_{\text{eff}} \approx 0.994$, with imaginary part less than 2.5×10^{-4}).

Therefore, we compute the effective relative permittivity as $\epsilon_{\text{eff}} \approx n_{\text{eff}}^2$, reported in Fig. 3. Notice how the different methods agree in the entire frequency region analyzed; around the resonance, they differ because mode analysis includes field retardation effects not accounted for in Maxwell Garnett formulation. Also, there is a frequency shift towards lower frequencies using MG with Mie theory with respect to MG with quasi static polarizability (Clausius Mossotti) as discussed in [48] and [21] for example.

3.1.2 Epsilon-near-zero region for silver shells

In this section, we are interested in alleviating the losses in a frequency region in which the real part of epsilon is close to zero (either negative or positive). By using the results shown in Sec. 3.1.1 for the structure in Fig. 1(a), we observe that the permittivity retrieved through mode analysis in Fig. 3(a) crosses zero at around 526 THz (570 nm), which overlaps well with the emission frequency of R6G. We then better analyze the frequency region 515-535 THz, and we consider 5 mM and 10 mM of R6G dye molecules in the dielectric core, optically pumped at 531 nm, with pumping rate $\Gamma_{\text{pump}} = 1.5 \times 10^9 \text{ s}^{-1}$. The real and the imaginary parts of the relative effective permittivity, obtained from mode analysis, are reported in Fig. 4. Notice from Fig. 4(b) how the imaginary part in presence of the gain material is reduced (red and green curves) with respect to the case in absence of the gain material (blue curve). Indeed, this demonstrates that the presence of R6G dye molecules allows for the alleviation of the losses, reaching a reduction of the extinction coefficient α_z / k_0 from 0.16 to 0.01 at $f = 526$ THz, in the epsilon-near-zero frequency band, for the highest concentration considered.

Fig. 4. (a) Real and (b) imaginary parts of the relative effective permittivity for the case in Fig. 3, obtained from mode analysis with polarizability in Eq. (3), in the epsilon-near-zero region around 526 THz.

3.2 Case with gold shells

In this section, we assume that Rhodamine 800 (R800) dye molecules are dispersed into the dielectric core as in Fig. 1(b), and we use the same four level system as in the previous example. According to [49,50], R800 has the following parameters: center emission frequency $f_a = 422$ THz (711 nm), wavelength linewidth is $\Delta\lambda_a = 26.7$ nm, and consequently $\Delta\omega_a = 2\pi\Delta\nu_a$, with frequency linewidth $\Delta\nu_a = c_0\Delta\lambda_a / \lambda_a^2 = 15.9$ THz. The pumping wavelength (between level 0 and level 3) is 680 nm (441 THz), and the decay rate from level 2 to level 1 is $1/\tau_{21}$, with $\tau_{21} = 500$ ps. Moreover, analogously to the previous example, we assume $\tau_{32} = \tau_{10} = 100$ fs. Also, we set the density of the dye molecules as

$\bar{N}_0 = 3 \times 10^{18} \text{ cm}^{-3}$, $\bar{N}_0 = 6 \times 10^{18} \text{ cm}^{-3}$ corresponding to about 5 mM and 10 mM, respectively. The coupling constant is $\sigma_a = 1.71 \times 10^{-7} \text{ C}^2/\text{kg}$ using $\gamma_{rad} = 4 \times 10^8 \text{ s}^{-1}$ (assuming a quantum yield of 0.2).

3.2.1 Mode analysis and effective parameters computation

We assume that the outer shell radius is $r_2 = 35 \text{ nm}$ (Fig. 1(b)), the dielectric core and surrounding environment are made by a material with $\epsilon_r = \epsilon_h = 2.25$, $r_1 = 30 \text{ nm}$ ($\rho \approx 0.86$), and $a = b = c = 100 \text{ nm}$. The shell is made of gold, whose Drude model parameters are $\epsilon_\infty = 9.5$, $\omega_p = 1.36 \times 10^{16} \text{ rad/s}$ and $\gamma = 1.05 \times 10^{14} \text{ s}^{-1}$ [51–53]. The core has a relative permittivity $\epsilon_1 = \epsilon_g / \epsilon_0$, with ϵ_g as in Eq. (14) with the parameters for R800. We use the nanoshell Mie electric polarizability expression in Eq. (3) for the results in Fig. 5. The real and the imaginary parts of the modal wavenumber in the 3D lattice, for transverse polarization, pertaining to modes traveling along the z direction, are shown in Fig. 5 for three different cases: (a) accounting for metal losses, (b) ideal lossless case (i.e., $\gamma = 0$ in Eq. (5)), and (c) in presence of gain (10 mM of R800 optically pumped at 680 nm with pumping rate $\Gamma_{\text{pump}} = 6.5 \times 10^9 \text{ s}^{-1}$).

Fig. 5. Wavenumber dispersion diagram versus frequency for T-pol for the structure in Fig. 1(b), using the polarizability in Eq. (3). (a) Real part and (b) imaginary part of the wavenumber $k_z = \beta_z + i\alpha_z$, for lossy, lossless and loss compensated cases.

As in Sec. 3.1.1, the effective refractive index of the homogenized array is retrieved from the wavenumber values reported in Fig. 5. The effective permeability (computed using Eq. (7)) is $\mu_{\text{eff}} \approx 1$ for the entire frequency region analyzed (the maximum deviation from 1 is at around 100 THz, where $\mu_{\text{eff}} \approx 0.99$, with imaginary part less than 1.7×10^{-3}). Therefore, we compute again the effective relative permittivity as $\epsilon_{\text{eff}} \approx n_{\text{eff}}^2$, reported in Fig. 6. Notice again the agreement between the different methods in the entire frequency region analyzed; around the resonance, they differ because mode analysis includes field retardation effects not accounted for in Maxwell Garnett formulation.

Fig. 6. (a) Real part and (b) imaginary part of the effective relative permittivity for the structure in Fig. 1(b) computed in three different ways: by Maxwell Garnett, by using the polarizability in Eq. (2) (MG - CM); the polarizability in Eq. (3) (MG - Mie); and mode analysis.

3.2.2 Epsilon-near-zero region for gold shells

We are again interested in alleviating propagation losses in a frequency region in which the real part of epsilon is close to zero (either negative or positive), as we attempted for the case with silver shell. By using the results shown in Sec. 3.2.1 for the structure in Fig. 1(b), we observe that the permittivity obtained from mode analysis in Fig. 6(a) crosses zero at around 421 THz (712 nm), which overlaps well with the emission frequency of R800. We then focus on the frequency region 400-440 THz, and we consider concentrations relative to 5 mM and 10 mM of R800 dye molecules in the dielectric core, optically pumped at 680 nm with pumping rate $\Gamma_{\text{pump}} = 6.5 \times 10^9 \text{ s}^{-1}$. The real and the imaginary parts of the relative effective permittivity, obtained from mode analysis, are reported in Fig. 7. Similarly to what described for the silver shell case in Sec. 3.1, it can be observed in Fig. 7(b) how the imaginary part in presence of the gain material is greatly reduced (red and green curves) with respect to the case in absence of the gain material (blue curve), showing that the presence of R800 dye molecules allows for the alleviation of the losses, reaching a reduction of the extinction coefficient α_z / k_0 from 0.37 to 7×10^{-4} at $f = 422$ THz, in the epsilon-near-zero frequency band, for the highest concentration considered.

Fig. 7. (a) Real and (b) imaginary parts of the relative effective permittivity for the case in Fig. 5, obtained from mode analysis with polarizability in Eq. (3), in the epsilon-near-zero region around 421 THz.

4. Conclusion

We have reported on the possibility of designing loss-compensated metamaterials, made of a 3D lattice of nanoshells, that exhibit epsilon near zero with moderate losses at optical frequencies by using optically pumped fluorescent dye molecules in the cores of the metamaterial constituent nanoshells. Indeed, we have been able to reduce the extinction coefficient α_z / k_0 from 0.16 to 0.01 in the epsilon-near-zero frequency band using dielectric-core silver-shell nanospheres in Fig. 1(a), and from 0.37 to 7×10^{-4} in the epsilon-near-zero frequency band using dielectric-core gold-shell nanospheres in Fig. 1(b), by using realistic parameters to model the emission of the dye molecules. However, high concentrations of dye molecules may impact in the overall compensation due to the presence of fluorescence quenching and other non-radiative phenomena. We assumed that the collection of the fluorescent dyes within the core can be approximated as an effective homogeneous material with gain that electrodynamically interacts with the metal nanoparticle. The quenching effect leads to a reduction of the gain in the system, and a treatment for each individual molecule-nanoparticle and molecule-molecule interaction is needed to estimate its real impact. Therefore, future work shall be devoted to optimization and also to experimental verification.

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