Composite material made of plasmonic nanoshells with quantum dot cores: loss-compensation and $\varepsilon$-near-zero physical properties

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Abstract
A theoretical investigation of loss-compensation capabilities in composite materials made of plasmonic nanoshells is carried out by considering quantum dots (QDs) as the nanoshells' cores. The QD and metal permittivities are modeled according to published experimental data. We determine the modes with real or complex wavenumber able to propagate in a 3D periodic lattice of nanoshells. Mode analysis is also used to assess that only one propagating mode is dominant in the composite material whose optical properties can hence be described via homogenization theory. Therefore, the material effective permittivity is found by comparing different techniques: (i) the mentioned mode analysis, (ii) Maxwell Garnett mixing rule and (iii) the Nicolson–Ross–Weir method based on transmission and reflection when considering a metamaterial of finite thickness. The three methods are in excellent agreement, because the nanoshells considered in this paper are very subwavelength, thus justifying the parameter homogenization. We show that QDs are able to provide loss-compensated $\varepsilon$-near-zero metamaterials and also loss-compensated metamaterials with large negative values of permittivity. Besides compensating for losses, the strong gain via QD can provide optical amplification with particular choices of the nanoshell and lattice dimensions.

(Some figures may appear in colour only in the online journal)

1. Introduction

In this paper we investigate the optical properties arising from composite materials made of plasmonic nanoshells. A comprehensive way to understand and classify collective resonances in such composite materials is by modal analysis [1–3] of a three-dimensional (3D) periodic structure as in figure 1. In particular, under certain circumstances of polarization and excitation, a 3D periodic lattice of plasmonic nanoshells with finite thickness could be described to a good approximation as a homogeneous slab with effective parameters, such as relative permittivity ($\varepsilon_{\text{eff}}$) and refractive index ($n_{\text{eff}}$). This effective medium representation allows for the generation of interesting physical properties at specific frequency bands, e.g. $\varepsilon$-near-zero (ENZ) metamaterials [4], cloaking [5] and ‘perfect lenses’ [6]. However, the metamaterial performance is usually affected and highly limited by the presence of large absorption losses. Therefore, loss-compensation mechanisms are inherently required to overcome this issue. Recently, active photonic materials such as fluorescent dye molecules, rare earth materials or quantum dots (QDs) have been proposed as a promising solution, because the gain experienced through the stimulated emission of an active medium is capable...
have been used in [18] to obtain loss-compensated negative permittivity at near-infrared. Realistic parameters of dye molecules (specifically Rhodamine 6G and Rhodamine 800) have been used in [3] to compensate for the losses in 3D periodic lattices of nanoshells, focusing on the generation of an ENZ metamaterial at optical frequencies. Here, besides using QDs instead of dye molecules as in [3], we also compare theoretical results, based on complex mode analysis, with full-wave electromagnetic simulation ones. There is still a lack of understanding regarding the usage of QDs for loss-compensation capabilities and on the possibility of using effective material parameters; thus, this paper aims at providing some physical insights.

2. Modes in the composite material

The nanoshells’ cores are assumed to be made of CdSe QDs surrounded by spacers (see figure 1) with matched relative permittivity \( \varepsilon_2 \) to avoid surface polarization screening charge [8, 19]. Assume then that the QD can be optically pumped to gain condition, such that the equivalent dielectric function \( \varepsilon_C \) of QD and spacer in the presence of gain, assumed to be homogeneous because \( r_2 \ll \lambda_{0,\text{min}} \), with \( \lambda_{0,\text{min}} \) the minimum free space wavelength, is calculated using the formalism in [8, 19, 20]. Accordingly

\[
\varepsilon_C = \varepsilon_2 + \frac{S_{\text{QD}}^2}{\omega^2 - \omega_C^2 + 12\omega\gamma_{\text{QD}}},
\]

where \( \omega_C = 2\pi f_C, f_C = 604 \text{ THz} \) is the emission frequency, \( \gamma_{\text{QD}} = 6.07 \times 10^{13} \text{ s}^{-1} \) is the broadening parameter, \( S = 0.53 \) the unitless transition strength and \( \varepsilon_2 = 10.2 \) (values taken from [8, 21] to match experimental results; we also assume that the QDs have the same radius as in [8] to emit at \( f_C = 604 \text{ THz} \)). The nanoparticles’ shells are assumed to be made of gold, whose relative permittivity \( \varepsilon_3 \) is described by interpolating the metallic bulk experimental results \( \varepsilon_{3\text{C}} \) from [22] with surface correction as [23, 24]

\[
\varepsilon_3 = \varepsilon_{3\text{C}} + \frac{\omega_{p}^2}{\omega^2 - \omega_{p}^2} - \frac{\omega_{c}^2}{\omega^2 - \omega_{c}^2},
\]

Here \( \omega_p = 1.36 \times 10^{19} \text{ rad s}^{-1} \) is the Drude plasma angular frequency, \( \gamma_D = 1.05 \times 10^{14} \text{ s}^{-1} \) is the Drude damping factor and \( \gamma_F = \gamma_{\text{QD}} + \gamma_F/(r_3 - r_2) \), with \( \gamma_F = 1.39 \times 10^6 \text{ m s}^{-1} \) the Fermi velocity, \( r_3 \) the shell outer radius, \( r_2 \) the spacer outer radius and \( r_3 - r_2 \) the metallic thickness. Equation (2) is implemented to avoid underestimation of gold losses when employing the Drude model. We model each nanoshell as a single electric dipole, using the single-dipole approximation (SDA) [1, 2, 25], for which the induced electric dipole moment is \( \mathbf{p} = \alpha_{ee} \mathbf{E}_{\text{loc}} \), with \( \alpha_{ee} \) the nanoshell electric polarizability (we use here the Mie expression reported in [3, 25]) and \( \mathbf{E}_{\text{loc}} \) the local field acting on it, produced by all the other scattering nanoshells. We determine the modes in the 3D lattice traveling along the \( z \) direction with wavenumber \( k_z = \beta_z + i\alpha_z \), which may assume real or complex values following the procedure described in [1–3]. In general, two modes with transverse polarization and one mode with longitudinal
polarization with moderately low attenuation constant $\alpha_z$ are present when spatial dispersion is not negligible \cite{2, 26, 27}. However, in all cases treated here, the size of the nanoshells is smaller than that of the nanoparticles in \cite{2, 3} and this implies that spatial dispersion is even lower than the already weak one observed in \cite{2, 3}. Basically, here only one dominant mode, whose electric polarization is in the direction transverse to the mode traveling in the $z$ direction, is propagating. However, a mode with longitudinal polarization with significantly small attenuation constant $\alpha_z$ may appear in a very narrow frequency range, where effective permittivity is vanishing, especially under the low-loss condition treated in this paper. It is therefore one of the purposes of this paper to check this peculiar condition and provide information about the polarization modes able to travel in the composite material. Accordingly, without loss of generality, we consider here the transverse polarization $p = p_x \hat{x}$ and the longitudinal polarization $p = p_z \hat{z}$. Under these assumptions, the modal wavenumbers are retrieved by solving the scalar equations:

$$A_{xx}(k_z) = 1 - \alpha_{ee} G_{xx}^\infty (r_0, r_0, k_z) = 0,$$

$$A_{zz}(k_z) = 1 - \alpha_{ee} G_{zz}^\infty (r_0, r_0, k_z) = 0,$$

for complex $k_z$ zeros. The terms $G_{xx}^\infty (r_0, r_0, k_z)$ and $G_{zz}^\infty (r_0, r_0, k_z)$ represent the $\hat{x}\hat{x}$ and $\hat{z}\hat{z}$ components, respectively, of the regularized periodic dyadic Green’s function \cite{2} and provide the field contribution evaluated at $r_0 = x_0 \hat{x} + y_0 \hat{y} + z_0 \hat{z}$ produced by all the nanoshells in the lattice except the one at $r_0$. To evaluate $G_{xx}^\infty (r_0, r_0, k_z)$ and $G_{zz}^\infty (r_0, r_0, k_z)$ we employ the Ewald method \cite{2, 28–32}, for it provides (i) rapid converging summations (i.e. only a handful of summation terms is needed to achieve convergence) and (ii) analytic continuation to the complex $k_z$ plane.

We analyze the physical properties of a lattice whose dimensions are chosen to achieve an ENZ metamaterial around the QD emission frequency when in gain condition: $r_1 = 2$ nm (same radius as in \cite{8}), $r_2 = 4$ nm, $r_3 = 8$ nm, $a = b = c = 21$ nm and a host with relative permittivity $\varepsilon_h = 2.25$. The modal wavenumber for the dominant propagating mode (i.e. the one that contributes mostly to the field in the 3D lattice, as discussed in \cite{2}) with transverse polarization in the case of (i) lossy (i.e. using equation (2)), (ii) lossless (i.e. $\text{Im}[\varepsilon_1] = 0$ artificially imposed) and (iii) loss-compensated lattices is reported in figure 2. At low frequencies, the real part of the modal wavenumber follows a typical dispersion curve around $k_c/\pi \approx 0.125$ (i.e. $f \approx 600$ THz): the adopted QDs provide a large gain (more than required for just loss-compensation). Thus the attenuation constant $\alpha_z$ becomes negative in a narrow frequency band, a symptom of optical amplification (see the discussion in section 3).

Other modes with transverse polarization, dramatically decaying because $\alpha_z \gg k$, and the symptom of a weak spatial dispersion, are present, but their effect can be neglected as discussed in \cite{2, 33}. For example, analogously to what was previously reported in \cite{2}, we also find a transversely polarized mode with backward propagation which, however, always has a large attenuation constant $\alpha_{ee}/c/\pi > 1$, even in the loss-compensated case and therefore it does not propagate.

The modal wavenumber $k_z = \beta_z + i\alpha_z$ for the mode with longitudinal polarization in the case of (i) lossy, (ii) lossless (i.e. $\text{Im}[\varepsilon_1] = 0$ artificially imposed) and (iii) loss-compensated lattices is reported in figure 3. In the lossy case, this modal wavenumber is mainly characterized by a large attenuation constant $\alpha_z$. In the lossless case, instead, this mode has a narrow propagation band with very small attenuation constant $\alpha_z$ at $k_c/\pi \approx 0.105$ (i.e. $f \approx 505$ THz), as also described in \cite{2}. Note that this narrow propagation band disappears when considering losses in the metal. At low frequencies, the loss-compensated case follows the lossy one. However, around $k_c/\pi \approx 0.125$ (i.e. $f \approx 600$ THz) the adopted QDs provide gain. Thus the attenuation constant $\alpha_z$ is smaller than in the lossy case, in a narrow frequency band. Nevertheless, the normalized attenuation $\alpha_z$ remains larger than 0.5 even at its lower value. In summary, this longitudinal mode in the loss-compensated case is always highly attenuated, even in the very narrow frequency region around $k_c/\pi \approx 0.125$, where $\alpha_z$ is still large, and therefore it does not contribute significantly to a field inside the lattice.

![Figure 2. Modal wavenumber dispersion diagram versus frequency for the dominant mode with transverse polarization. (a) Real part and (b) imaginary part of the wavenumber $k_z = \beta_z + i\alpha_z$ for lossy, lossless and loss-compensated cases.](image)
It is also interesting to note that the propagation constant $\beta_z$ of this longitudinal mode becomes negative, a symptom of backward propagation, not allowed in standard 3D lattices [2, 26, 27].

3. Loss-compensation and electric permittivity

As previously mentioned, we are interested in generating a loss-compensated ENZ metamaterial as in [3], and also in showing the possibility of achieving large negative values of $\varepsilon_{\text{eff}}$ with low losses. The results in section 2 have shown that one mode only, with transverse polarization, is able to propagate inside the lattice, and therefore the composite material is now considered for permittivity homogenization. We retrieve the effective permittivity by using three different methods: (i) modal analysis (Mode-SDA), (ii) Maxwell Garnett (MG) homogenization theory and (iii) the Nicolson–Ross–Weir (NRW) retrieval method from reflection $R$ and transmission $T$ of finite thickness structures, here computed using a HFSS full-wave simulation. Note that, when employing MG and NRW methods, it is implicitly assumed that only one propagating mode is dominant, and this has been verified by mode analysis. The comparison among the different methods is performed because their agreement confirms the validity of the homogeneous treatment of the composite material. For brevity, we direct the reader to [2, 3] and references therein for guidelines on how to choose $q$ and $+$/$-$ in equation (5). Then, one can easily retrieve $\varepsilon_{\text{eff}} \approx n_{\text{eff}}^2$. In general, the NRW solution should be proven to be consistent for varying the number of layers $N$, as shown in [2] for example. For simplicity in figures 4 and 5 we show only the result with $N = 4$, because results with other $N$ values are found to be in good agreement.

The effective relative permittivity of the homogenized metamaterial discussed in section 2 is reported in figures 4(a) (real part) and (b) (imaginary part) in the presence of gain; the same result in the absence of gain is shown as a dotted black line. The comparison with the different retrieval methods, performed only in the case of gain for clarity of the results, shows very good agreement. Modal analysis usually provides more accurate results than Maxwell Garnett theory around the nanoparticle resonance frequency because it includes all the field retardation effects and all nanoparticle interactions. Since modal analysis is here based on the SDA, full-wave NRW-HFSS is expected to be the most effective method for those frequencies.
Indeed, the maximum value assumed by the normalized $\beta$ is very subwavelength with respect to any guided wavelength. However, here the nanoshells and the lattice period are accurate among the three methods for parameter retrieval. Nonetheless, this result shows the possibility to tailor the effective permittivity to approach virtually zero in the ENZ region. In both cases A and B in figure 6, the loss-compensated metamaterial has $\text{Im}[\varepsilon_{\text{eff}}]$ that never assumes negative values. The metamaterial also exhibits a frequency band where the effective permittivity is large, negative and with very low losses.

In conclusion, we have shown the possibility to tailor the effective permittivity to approach virtually zero losses in an ENZ frequency band by using small nanoshell filling fraction in the composite $f_{\text{vol}} = 4\pi r_3^3/(3abc)$. Two illustrative examples are shown in figure 7, where we analyze the loss-compensation property when varying certain physical dimensions of the 3D lattice as follows, and keeping the others as in section 2: (A) $r_3 = 9$ nm and $f_{\text{vol}} = 44\%$, and (B) $r_2 = 11$ nm, $r_3 = 23$ nm and $f_{\text{vol}} = 50\%$. In both cases, two frequency bands with interesting physical properties can be observed: (i) ENZ behavior in the range 550–590 THz (frequency band of about 40 THz) and (ii) negative permittivity in the range 585–600 THz. We have observed that by varying the filling factor one can tune the permittivity values in the ENZ region. In both cases A and B in figure 7, the presence of gain (solid curves) greatly reduces the value of $\text{Im}[\varepsilon_{\text{eff}}]$ compared to the results without gain (dotted curves), without assuming negative values. Regarding case A, losses have been highly compensated in a wide frequency band, i.e. 530–595 THz, with respect to the case without gain. Case B exhibits a better loss-compensation than Case A in a wider frequency band. Both configurations A and B also exhibit negative $\text{Re}[\varepsilon_{\text{eff}}]$ with very low losses at optical frequencies.

4. Conclusions and final remarks

In conclusion, we have shown the possibility to tailor the effective permittivity to approach virtually zero losses in an ENZ frequency band by using small nanoshell filling fraction in the composite $f_{\text{vol}} = 4\pi r_3^3/(3abc)$.
particles, thus creating favorable conditions for a number of applications, including low-threshold nonlinear effects [34]. Moreover, we have observed the generation of negative effective permittivity with low losses to be possible as well. Besides loss-compensation capabilities, the strong gain via QD can provide optical amplification with particular choices of the nanoshell and lattice dimensions, although the relation between possible instabilities and an overall gain should be further studied. These conditions have been obtained by using cores with QDs whose emission band overlaps with that where the 3D lattice exhibits low values of \( \text{Re}[\varepsilon_{\text{eff}}] \). In other words, the emission band of the QD cores has been chosen slightly higher than the collective plasmonic resonance frequency of the 3D lattice. One can, however, foresee other possible loss-compensation arrangements that will be studied in future work. For example, QDs can be arranged around a nanosphere or nanoshell as shown experimentally in [35, 36]. That structure would represent a good candidate for loss-compensation studies in optical metamaterials which would, however, require accounting for the nanoshell–QD and QD–QD interactions. The high gain provided by QDs have permitted us to consider nanoshells with very subwavelength dimensions and therefore the electric properties of the composite material can be well described using homogenization techniques.

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References

[1] Steshenko S and Capolino F 2009 Single dipole approximation for modeling collections of nanoscatteçers Theory and Phenomena of Metamaterials ed F Capolino (Boca Raton, FL: CRC Press) p 8.1
[2] Campione S, Steshenko S, Albani M and Capolino F 2011 Opt. Express 19 26027–43
[3] Campione S, Albani M and Capolino F 2011 Opt. Mater. Express 1 1077–89
[4] Garcia N, Ponziovska E V and Xiao J Q 2002 Appl. Phys. Lett. 80 1120–2
[5] Schurig D, Mock J J, Justice B J, Cummer S A, Pendry J B, Starr A F and Smith D R 2006 Science 314 977–80
[6] Pendry J B 2000 Phys. Rev. Lett. 85 5966
[7] Dulkeith E, Moretani A C, Niedereichholz T, Klar T A, Feldmann J, Levi S A, van Veggel F C J M, Reinhoudt D N, Möller M and Gittins D I 2002 Phys. Rev. Lett. 89 203002
[8] Webb K J and Ludwig A 2008 Phys. Rev. B 78 153503
[9] Binetti E, Ingrosso C, Striccoli M, Cosma P, Agostiano A, Pataky K, Brugger J and Curri M L 2012 Nanotechnology 23 075701
[10] Strangi G, De Luca A, Ravaine S, Ferrie M and Bartolini R 2011 Appl. Phys. Lett. 98 251912
[11] De Luca A, Grzelczak M P, Pastoriza-Santos I, Liz-Marzán L M, La Deda M, Striccoli M and Strangi G 2011 ACS Nano 5 5823–9
[12] Xiao S, Drachev V P, Kildishev A V, Ni X, Chettiar U K, Yuan H-K and Shalaev V M 2010 Nature 466 735–8
[13] Gordon J A and Ziolkowskki R W 2008 Opt. Express 16 6692–716
[14] Fu Y, Thylén L and Ågren H 2008 Nano Lett. 8 1551–5
[15] Bratkovsky A, Ponziovska E, Wang S-Y, Holmstrom P, Thylén L, Fu Y and Ågren H 2008 Appl. Phys. Lett. 93 193106
[16] Mackay T G and Lakhtaka A 2009 Opt. Commun. 282 2470–5
[17] Ciuttoni A, Marinelli R, Rizza C and Palange E 2011 [ε]-near-zero materials in the near-infrared, arXiv:1107.5540
[18] Zeng Y, Wu Q and Werner D H 2010 Opt. Lett. 35 1431–3
[19] Holmstrom P, Thylén L and Bratkovsky A 2010 J. Appl. Phys. 107 064307
[20] Holmstrom P, Thylén L and Bratkovsky A 2010 Appl. Phys. Lett. 97 073110
[21] Murray C B, Kagan C R and Bawendi M G 2000 Annu. Rev. Mater. Sci. 30 545–610
[22] Johnson P B and Christy R W 1972 Phys. Rev. B 6 4370
[23] Averitt R D, Westcot t S L and Halas N J 1999 J. Opt. Soc. Am. B 16 1824–32
[24] Peña O, Pal U, Rodríguez-Fernández L and Crespo-Sosa A 2008 J. Opt. Soc. Am. B 25 1371–9
[25] Bohren C F and Huffman D R 1983 Absorption and Scattering of Light by Small Particles (New York: Wiley)
[26] Silveirinha M G 2007 Phys. Rev. B 76 245117
[27] Alù A and Engheta N 2007 Phys. Rev. B 75 024304
[28] Ewald P P 1921 Ann. Phys. (Berlin) 64 253–87
[29] Ham F S and Segall B 1961 Phys. Rev. 124 1786
[30] Stevanovic I and Mosig J R 2007 Microw. Opt. Tech. Lett. 49 1353–7
[31] Lovat G, Burghignoli P and Araneo R 2008 IEEE Trans. Microw. Theory Tech. 56 2069–75
[32] Kustepeli A and Martin A Q 2000 IEEE Microw. Guided Wave Lett. 10 168–70
[33] Campione S, Lannebere S, Aradian A, Albani M and Capolino F 2012 J. Opt. Soc. Am. B in press
[34] Vincenti M A, de Ceglia D, Ciuttoni A and Scalora M 2011 Phys. Rev. A 84 063826
[35] Liu N, Prall B S and Klimov V I 2006 J. Am. Chem. Soc. 128 15362–3
[36] Fanizza E, Malaquin L, Kraus T, Wolf H, Striccoli M, Miccoli N, Taurino A, Agostiano A and Curri M L 2010 Langmuir 26 14294–300