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$|\epsilon|$-Near-zero materials in the near-infrared

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Abstract We consider a mixture of metal-coated quantum dots dispersed in a polymer matrix and, using a modified version of the standard Maxwell-Garnett mixing rule, we prove that the mixture parameters (particles radius, quantum dots gain, etc.) can be chosen so that the effective medium permittivity has an absolute value very close to zero in the near-infrared, i.e. $|\mathrm{Re}(\epsilon)| \ll 1$ and $|\mathrm{Im}(\epsilon)| \ll 1$ at the same near-infrared wavelength. Resorting to full-wave simulations, we investigate the accuracy of the effective medium predictions and we relate their discrepancy with rigorous numerical results to the fact that $|\epsilon| \ll 1$ is a critical requirement. We show that a simple method for reducing this discrepancy, and hence for achieving a *prescribed* and very small value of $|\epsilon|$, consists in a subsequent fine-tuning of the nanoparticles volume filling fraction.

1 Introduction

Epsilon-near-zero (ENZ) materials have attracted much attention in the last decade for their intriguing optical properties [1]. The $|\epsilon|$-near-zero condition $|\epsilon| \ll 1$ (where both real and imaginary parts of the dielectric permittivity are very small) have suggested novel ways to achieve remarkable effects like transmissivity directional hysteresis [2], peculiar plasmonic memory functionalities and bistability [3] and highly efficient second-harmonic generation [4]. All of these intriguing effects are consequences of the fact that, in the presence of the very small permittivity background, nonlinearity is no longer a perturbation thus disclosing a novel and highly nonlinear optical behavior. The scenario is additionally supplied by a novel kind of field enhancement consisting in the fact that, in the transverse magnetic configuration, the longitudinal component of the electric field becomes singular at the interface between vacuum and the $|\epsilon|$-near-zero medium, due to the continuity of the displacement field component normal to the interface [5]. So it is quite natural to ask: to what extent can we realize a $|\epsilon|$-near-zero material at the prescribed optical wavelength?

It is well-known that standard ENZ materials with the less restrictive condition $\mathrm{Re}(\epsilon) \simeq 0$ are directly available in nature. Main examples are low-loss metals (like Au and Ag) whose Drude-type dispersion behavior is such that, close to their ultra-violet plasma frequency, the real part of the dielectric permittivity is very small [6]. In addition heavily doped semiconductors as ITO, GZO and AZO have Drude-type dispersion behavior as well (transparent conductors) and they can be doped to tune their plasma frequency to point of achieving the condition $\mathrm{Re}(\epsilon) \simeq 0$ at telecom wavelengths [8]. On the other hand there are semiconductors exhibiting Lorentz-type dispersion behavior as, for example, GaP, GaAs, and Si for which the condition $\mathrm{Re}(\epsilon) \simeq 0$ occurs in the ultra-violet [7]. In the visible range natural ENZ materials are lacking, so that the engineering of metal-based composite materials is required for filling this gap [9–11]. In the context of metamaterials, the condition $\mathrm{Re}(\epsilon) \simeq 0$ can be achieved at

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a prescribed wavelength by suitably designing the composite which has to comprise both positive and negative permittivities. In addition, if among the metamaterial constituents there is a gain medium, even the imaginary part of the effective permittivity can be managed [12–15] and this is a basic ingredient for achieving the $|\epsilon|$-near-zero condition. Campione et al. have considered a 3D periodic array of metallic-shell nanospheres with fluorescent dyes embedded in the nanoshells' dielectric cores [16] and they have theoretically predicted that the structure behaves as low loss epsilon-near-zero metamaterials if their design is such that the epsilon-near-zero frequency region overlaps with the emission band of the adopted gain media. An efficient gain mechanism in the near infrared is provided by quantum dots and they have been exploited by several authors to design lossless metamaterials [17, 18]. Rizza et al. have shown that a gain-assisted metallo-dielectric nano-laminate can be designed to fulfil the $|\epsilon|$-near-zero condition at visible frequencies [11], the loss compensation being achieved by incorporating optically pumped dye molecules (with a resonance wavelength of $\lambda = 610$ nm) in the dielectric layers.

In this paper we show that the condition $|\epsilon|$-near-zero can be achieved in the near-infrared through a composite material obtained by dispersing silver-coated PbSe/ZnSe quantum dots within a polymer (PMMA) matrix (see Fig. 1a). Exploiting a modified version of the Maxwell-Garnett mixing rule which additionally accounts for the geometry of the structured nanoparticles [17], we tailor the mixture properties (e.g. the core and shell radii and the quantum dot gain) so that both the real and imaginary of the effective permittivity are very close to zero at the same near-infrared wavelength. It is worth noting that $|\epsilon| \ll 1$ is a very critical condition, the actual fulfilling of a *prescribed* very small value of the dielectric permittivity being a highly nontrivial task. Most of the paper dealing with epsilon-near-zero media are focused on showing that a frequency exists at which the real part of the composite effective permittivity changes sign. However, little effort is devoted at achieving a *prescribed* very small value of the effective permittivity at a *prescribed* frequency, an important target which is essential for many applications [2–5]. Generally, in an actual manufactured sample, a variety of generally minor effects (departure from homogeneous behavior, spatial nonlocal effects, surface contributions, etc.) can produce a large relative deviation of the dielectric permittivity from the very small value predicted by the effective medium theory. Therefore, we have performed rigorous full-wave simulations to investigate the actual feasibility of the $|\epsilon|$-near-zero condition in a slab filled by the proposed mixture. It turns out that the dielectric permittivity predicted by full-wave simulations is very small and of the some order of magnitude of that predicted by the effective medium approach, the relative discrepancy being however significant. On the other hand we show that such a discrepancy can be reduced by means of a further designing stage, which consists in slightly adjusting the nanoparticle volume filling fraction.

2 Effective medium description

Within the context of the effective medium approach, if the radiation wavelength is much greater that the nanoparticle radius, we can regard the silver-coated spherical PbSe/ZnSe quantum dots as an effective homogeneous sphere whose equivalent permittivity is [17]

$$\epsilon_s = \epsilon_{\mathrm{Ag}} \frac{\epsilon_{\mathrm{QD}}(1+2\rho) + 2\epsilon_{\mathrm{Ag}}(1-\rho)}{\epsilon_{\mathrm{QD}}(1-\rho) + \epsilon_{\mathrm{Ag}}(2+\rho)}, \qquad (1)$$

where $\rho = r_{\mathrm{QD}}^3 / r_{\mathrm{Ag}}^3$ is the fraction of the total particle volume occupied by the inner material sphere (r_{QD} and r_{Ag} are the inner and the outer shell radii, respectively, see Fig. 1a), whereas ϵ_{Ag} and ϵ_{QD} are the PbSe/ZnSe quantum dot core and silver shell permittivities, respectively. Here, the silver and the PbSe/ZnSe quantum dots dispersion behaviors are described by the Drude and Lorentz-Drude model, respectively, i.e. $\epsilon_{\mathrm{Ag}} = \epsilon_\infty - \omega_p^2/(\omega^2 + i\omega\Gamma)$ and $\epsilon_{\mathrm{QD}} = \epsilon_b + A\omega_0^2/(\omega^2 - \omega_0^2 + i2\omega\gamma)$, where $\epsilon_\infty = 4.56$, $\omega_p = 13.8 \times 10^{15}$ Hz, $\Gamma = 0.3 \times 10^{15}$ Hz, $\epsilon_b = 12.8, \omega_0 = 2.27 \times 10^{15}$ Hz, $\gamma = 1.51 \times 10^{12}$ Hz [18] and A is a dimensionless parameter related to the gain efficiency of the considered quantum dot. Note that the quantum dots resonant wavelength is $\lambda_0 = (2\pi c)/\omega_0 = 827$ nm so that the mixture is adequate to be tailored in the near-infrared. Exploiting the Maxwell-Garnett approach, the effective

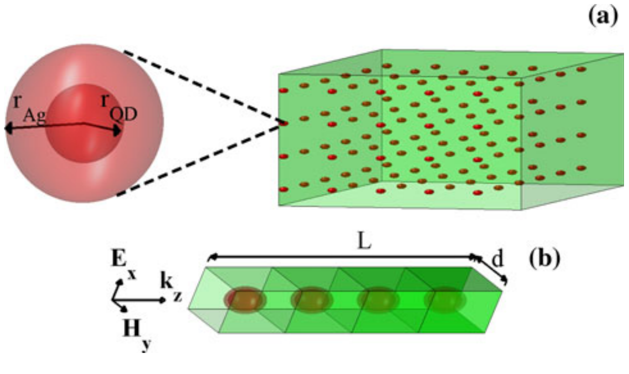

Fig. 1 **a** Sketch of the considered composite material obtained by dispersing silver-coated PbSe/ZnSe quantum dots within a polymer (PMMA) matrix. Here r_{Ag} and r_{QD} are the outer and inner radii of the nanoparticle silver shell, respectively. **b** Sketch of the impinging field geometry and of the integration domain used for the full-wave analysis

dielectric permittivity of the polymer (PMMA) matrix hosting the dispersed metal-coated quantum dots is

$$\epsilon = \epsilon_h \frac{\epsilon_s(1+2f) + 2\epsilon_h(1-f)}{\epsilon_s(1-f) + \epsilon_h(2+f)}, \qquad (2)$$

where f is the nanoparticle volume fraction and $\epsilon_h = 2.202$ is the PMMA permittivity. Aimed at achieving very small values of both $|\mathrm{Re}(\epsilon)|$ and $|\mathrm{Im}(\epsilon)|$ at the same wavelength $\lambda_0 = 827$ nm, we have performed a detailed scan of the multidimensional parameter space comprising core and nanoparticle radii, volume filling fraction and QD gain efficiency. As a result, for the geometrical parameters $r_{\mathrm{QD}} = 5$ nm, $r_{\mathrm{Ag}} = 6.23$ nm ($\rho = 0.52$) and the volume filling fraction $f = 0.1$, the effective medium approach of Eqs. (1) and (2) yields $\epsilon = 0.01$ ($\mathrm{Im}(\epsilon) = 0$) at $\lambda = 827$ nm for $A = 0.003$. In Fig. 2, we report the real (panel a) and imaginary (panel b) parts of the effective dielectric permittivity ϵ of Eq. (2) (solid line), as a function of λ in a spectral range around the quantum dots resonant wavelength λ_0. We conclude that the proposed mixture can actually be tailored to fulfill the $|\epsilon|$-near zero condition.

3 Full wave simulations

In most of the proposed configurations [2, 3], the $|\epsilon|$-near-zero condition is not exploited for representing the limiting theoretical situation where the permittivity strictly vanishes ($\epsilon = 0$) but the actual numerical small value of $|\epsilon|$ plays a fundamental role since it tunes various effects and field enhancements [4, 5]. It should be noted that manufacturing an actual sample exhibiting the prescribed small value of $|\epsilon|$ can be a very nontrivial task since a variety of generally minor effects (departure from homogeneous behavior, spatial nonlocal effects, surface contributions, etc.) can produce a large relative deviation of the dielectric permittivity from the very small value predicted by the effective medium theory. In order to investigate the actual feasibility of the proposed $|\epsilon|$-near-zero mixture, we have performed 3D finite-element full-wave simulations for evaluating the transmission coefficient of a slab filled with the proposed mixture and consequently retrieving its effective dielectric permittivity. More precisely, we have considered a parallelepiped of height $L = 86.49$ nm of equal width and thickness $d = 21.6$ nm (see Fig. 1b), containing four metal-coated quantum dots aligned along the z axis and we have adopted periodic boundary conditions along the surfaces parallel to the z axis. Two layers of unit permittivity (vacuum) have been located on the top and bottom faces of the parallelepiped for providing normal incidence illumination with monochromatic light and for collecting the transmitted field. Accordingly, at entrance and exit faces (orthogonal to the z axis) of the integration domain, standard scattering condition for plane waves propagating along the z axis have been used. It is worth noting that we have set all the geometrical sizes of the objects within the integration domain to coincide with those employed in the above described effective medium analysis. In Fig. 2, in addition to the effective medium approach results (solid lines), we have plotted the real and imaginary parts of the dielectric permittivity retrieved from full-wave simulations (dashed lines) and we note that there is a very good global agreement between theoretical predictions and numerical results. On the other hand it is evident from the insets of panels (a) and (b) of Fig. 2, that in the spectral range around the $\mathrm{Re}(\epsilon) = 0$ crossing point, the *relative* discrepancy $(\Delta|\epsilon|)/|\epsilon|$ is significant since, for example, at $\lambda = 827$ nm, full-wave analysis yields $|\epsilon| = 0.07$ (see panel a of Fig. 3) that is seven times larger than the expected value $|\epsilon| = 0.01$. Such a discrepancy is unavoidable as it results from all the physical effects and mechanisms neglected by the effective medium theory as well as from the numerical error accompanying the full-wave simulations. However, we here point out that in the design of the actual medium, such a discrepancy can be essentially reduced by means of a second-stage parameter refining which consists in fine-tuning the nanoparticle volume filling fraction. In Fig. 3b, we plot the $|\epsilon|$ retrieved from further full-wave simulations that we have performed at the wavelength $\lambda = 827$ nm for different nanoparticle volume filling fraction f. We note that the requirement $|\epsilon| = 0.01$ is attained for $f = 0.105$, i.e. a slight change of f allows the actual mixture to exhibit the required value of $|\epsilon|$ at the specified wavelength. Even though the refined value of $f = 0.105$ slightly differs from the starting value $f = 0.1$, it should be stressed that such a second-stage

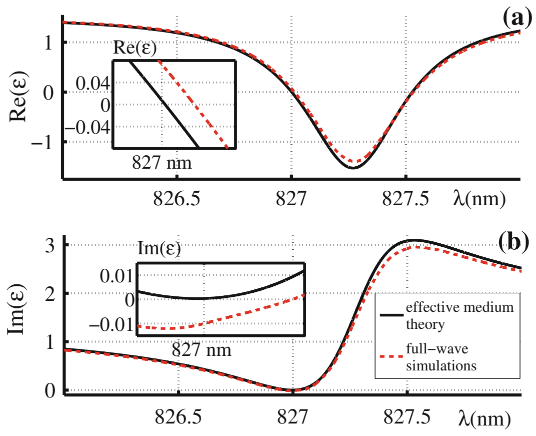

Fig. 2 Real (**a**) and imaginary (**b**) parts of the composite dielectric permittivities evaluated through the effective medium approach of Eq. (2) (*solid lines*) and retrieved from the full-wave simulations (*dashed lines*) as functions of the wavelength λ. The *insets* of panels **a** and **b** are magnified copies of the corresponding panels for wavelengths close to $\lambda = 827$ nm

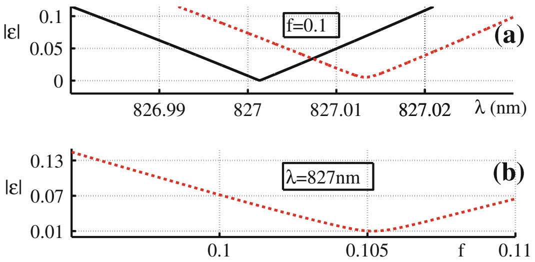

Fig. 3 **a** Moduli of the theoretical effective dielectric permittivity evaluated from Eq. (2) (*solid line*) and retrieved from full-wave simulations (*dashed line*) as functions of the wavelength λ. **b** Modulus of the dielectric permittivity retrieved from full-wave simulations as a function of the nanoparticle volume filling fraction *f*

parameter refinement is conceptually essential to our discussion since it suggest a way for achieving *the prescribed* very small value of the dielectric permittivity in actual experimental samples. In fact, the numerical refinement of the parameters suggests that, by alternating sample preparation stages and experimental dielectric permittivity retrieval stages, the manufacturer can in principle obtain the prescribed and very small value of $|\epsilon|$ after few cycles.

4 Conclusion

In conclusion, we have exploited the optical properties of a mixture of metal-coated quantum dots dispersed in a polymer matrix to prove that, by suitably choosing its geometrical parameters, it is possible to achieve a very small value of the absolute value of the permittivity at an infrared wavelength. We believe that the realization of a material exhibiting the $|\epsilon|$-near-zero property in the near-infrared or in the visible range is a very important target of photonics since the very small permittivity would allow any possible permittivity change (which is generally a small perturbation) to play a fundamental role on electromagnetic propagation. As a consequence, $|\epsilon|$-near-zero materials are expected to offer very original ways for achieving efficient optical steering (via optical nonlinearity) and externally driven manipulation (via electro-optic effect, acousto-optic effect, etc.) and hence for designing a future generation of photonic and nano-photonic devices.

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