Electrostatic theory for designing lossless negative permittivity metamaterials

Yong Zeng, Qi Wu and Douglas H. Werner

Department of Electrical Engineering, Pennsylvania State University, State College, Pennsylvania 16802

In this Letter, we develop an electrostatic theory for designing bulk composites with effective lossless negative permittivities. The theory and associated design procedure are validated by comparing their predictions with those of rigorous full-wave simulations. It is demonstrated that the excitation of the Fröhlich mode (the first-order surface mode) of the constitutive nanoparticles plays a key role in achieving negative permittivities with compensated losses. © 2010 Optical Society of America

OCIS codes: 220.1080, 240.6680, 350.4990
Metamaterials with simultaneous negative permeability and permittivity have attracted much attention in the last decade [1–4]. Such novel media are absent in nature and have potential applications such as perfect imaging [5] and optical cloaking [6–8] as well as other transformation optical devices [9, 10]. Unfortunately, the intrinsic ohmic loss of plasmonic nanostructures seriously deteriorates their performance. To alleviate metal absorption loss, metamaterials containing gain media have been proposed [11–18]. For instance, a recent experiment found that 44-nm-diameter coated spheres with a gold core and dye-doped silica shell can amplify light at a wavelength of 531 nm [14].

In accordance with the definition of refractive index $n$, a negative value of $n$ requires simultaneous negative dielectric permittivity $\varepsilon$ and magnetic permeability $\mu$. Searching for materials with negative dielectric constant and compensated loss is therefore extremely important. As the first attempt, Fu et al. suggested metamaterials comprised of binary metal and semiconductor quantum dots (with optical gain) [19–21], numerically demonstrating that these composites indeed possess an effective negative real-valued $\varepsilon$ at specific frequencies. However, the underlying physical mechanisms that governs this class of novel materials have not been fully explained, nor is there an easy-to-use design procedure. In this Letter, we employ nanoparticles to build up a bulk composite with lossless negative permittivity, and develop an electrostatic theory to illustrate the underlying physics. We find that the crucial requirement is the excitation of the first-order surface mode of the constitutive nanoparticles. Consequently, these particles present localized surface plasmon singularities [22], which further result in extremely high enhancement of local field intensity as well as surface-enhanced Raman scattering [23].

We start by considering a coated sphere with inner radius $r_1$ and outer radius $r_2$, surrounded by a homogenous medium that has a positive real-valued permittivity $\epsilon_m$. Its electromagnetic response can be described by a rigorous dynamic theory developed almost 60 years ago [24]. When the incident wavelength is much larger than the size of the particle, this coated sphere can be approximated as an ideal dipole with polarizability [25]

$$\alpha = 4\pi r_2^3 \frac{(\epsilon_2 - \epsilon_m)(\epsilon_1 + 2\epsilon_2) + \rho(\epsilon_1 - \epsilon_2)(\epsilon_m + 2\epsilon_2)}{(\epsilon_2 + 2\epsilon_m)(\epsilon_1 + 2\epsilon_2) + 2\rho(\epsilon_2 - \epsilon_m)(\epsilon_1 - \epsilon_2)},$$

where $\rho = r_1^3/r_2^3$ is the fraction of the total particle volume occupied by the inner sphere material, while $\epsilon_1$ and $\epsilon_2$ are the permittivity of the core and shell, respectively. We further recall that a homogeneous sphere in the electrostatics approximation can also be treated as an ideal dipole with polarizability [25]

$$\alpha = 4\pi r^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m},$$

with $r$ being the radius and $\epsilon$ being the permittivity. Consequently, a coated sphere can be
approximated as an effective homogeneous sphere with an equivalent permittivity given by

$$\epsilon_c = \frac{\epsilon_1 (1 + 2\rho) + 2\epsilon_2 (1 - \rho)}{\epsilon_1 (1 - \rho) + \epsilon_2 (2 + \rho)},$$  \hspace{1cm} (3)$$

which bears a resemblance to the standard Maxwell-Garnett mixing rule for a heterogeneous medium where homogeneous spheres are dilutely mixed into an isotropic host environment \[26\]. It should be emphasized that this equivalent permittivity can be derived directly by solving Laplace’s equation of electrostatics together with proper boundary conditions \[26\].

For a bulk material consisting of these nanoparticles, its effective electrostatic permittivity is determined by the Clausius-Mossotti relation, also known as the Lorentz-Lorenz formula \[26–28\],

$$\epsilon_b = \frac{4\pi r^3 \rho^2 + 2f\alpha}{4\pi r^3 - f\alpha},$$  \hspace{1cm} (4)$$

where \(f\) is the filling fraction of the composite. Substituting \(\alpha\) with Eq. (2), the above expression can be rewritten as

$$\epsilon_b = \frac{\epsilon_m \epsilon_c (1 + 2f) + 2\epsilon_m (1 - f)}{\epsilon_c (1 - f) + \epsilon_m (2 + f)}.$$  \hspace{1cm} (5)$$

Once again, this effective permittivity has an expression identical to the standard Maxwell-Garnett formula.

A lossless dielectric constant \(\epsilon_b\) must be entirely real, which leads to the condition that

$$\text{Im}(\epsilon_c) = 0$$  \hspace{1cm} (6)$$

implying that the absorption cross section of the nanoparticle is always zero \[26\]. The particle therefore must contain a medium with gain to compensate for the ohmic losses of the metal. Requiring \(\epsilon_b\) to be negative results in

$$\frac{\epsilon_m 2 + f}{f - 1} < \text{Re}(\epsilon_c) < \frac{\epsilon_m 2f - 2}{1 + 2f}.$$  \hspace{1cm} (7)$$

The real part of \(\epsilon_c\) is negative since the filling fraction \(f\) is always smaller than unity. Furthermore, the left-hand expression is a strictly decreasing function with a maximum of \(-2\epsilon_m\) at \(f = 0\), while the expression on the right-hand side is a monotonically increasing function with a minimum of \(-2\epsilon_m\). \text{Re}(\epsilon_c) therefore should be tuned to around \(-2\epsilon_m\) so that the filling fraction \(f\) can be modest. The combination of Eq. (6) and Eq. (7), i.e., \(\epsilon_c = -2\epsilon_m\), is actually the Fröhlich mode (the first-order surface mode) condition for the individual particle \[29\]. More specifically, the denominator of the electric dipolar polarizability (see Eq. (2)) goes to zero at the Fröhlich frequency. The first-order scattering coefficient of the nanoparticle is therefore infinite without accounting for saturation effects, which results in an
infinite scattering cross section. This phenomenon was recently named the surface plasmon singularity [12, 22, 25].

Although the above conclusion is derived from coated spheres, it can be extended to general nanoparticles with arbitrary shapes. As suggested by the Clausius-Mossotti relation, the electric dipolar polarizability $\alpha$ should be large enough to achieve a negative real-valued $\epsilon_b$ which is weakly dependent on the filling fraction. We recall that $\alpha$ is infinite at the Fröhlich frequency. Therefore we need to excite the first-order surface mode of the constitutive nanoparticles to tune the effective permittivity of the bulk composite to be real and negative. It should be mentioned that, accompanied by the surface mode, the electromagnetic field is strongly localized around the nanoparticle, which further greatly enhances the Raman scattering signals [23].

We can now design bulk composites with negative real-valued dielectric constants. A first example consists of silver coated spherical semiconductor quantum dots (QDs). Specifically, we employ similar QDs to those in Ref. [19] whose permittivity is described by a realistic two-level model [19–21],

$$\epsilon_{\infty} - \frac{\beta}{\omega_0 - \omega - i\gamma},$$

where the parameters are given by $\epsilon_{\infty} = 12.8$, $\hbar\omega_0 = 1.5$ eV ($\lambda = 827$ nm), $\hbar\gamma = 1$ meV and $\beta/\gamma = 100$ [19]. In addition, the relative dielectric constant of silver is fitted by the Drude model of $4.56 - \omega_p^2/(\omega^2 + i\gamma\omega)$, with $\omega_p = 1.4 \times 10^{16}$ s$^{-1}$ and $\gamma = 1.0 \times 10^{14}$ s$^{-1}$ [30]. Furthermore, the radius of the spherical QD is 5 nm, and the silver shell has a thickness of 2.25 nm. Using Eq. (3), the permittivity of an individual particle $\epsilon_c$ is computed and the result is plotted in Fig. 1(a). Around a wavelength of 822 nm, the curve of $\text{Im}(\epsilon_c)$ passes through zero (marked with the dotted line), and $\text{Re}(\epsilon_c)$ is close to $-2.0$, showing that the first-order surface mode is excited. To elucidate its characteristics, the corresponding local optical field is plotted in Fig. 1(c). It shows a uniform field distribution inside the core and hot spots with strong electric field at the poles outside the shell. In other words, light is significantly enhanced around the nanoshell. Using Eq. (5), we further compute the effective permittivity $\epsilon_b$ of a bulk composite with a filling fraction of 0.1; Fig. 1(b) shows the result. Indeed, a lossless $\epsilon_b = -2.0$ is found at 821.8 nm wavelength. To verify the electrostatic result, we consider the coated spheres in a simple cubic lattice with lattice spacing of 20 nm. A full-wave finite-element simulation is then used to calculate the corresponding scattering matrix [31], and the transmission/reflection method is finally applied to extract the effective permittivity [32, 33]. The result is plotted in Fig. 1(b) with dotted curves, and is found to be in perfect agreement with its analytical counterpart.

A second example is inspired by the active gold nanobox studied in Ref. [23]. By embedding a gain medium in the core, this cubic particle is found to extremely enhance local electric intensity so that single-molecule detection is achievable through surface-enhanced Raman
scattering [23]. Although the underlying mechanism was not demonstrated in the original literature, it is quite possible that it is related to the first-order surface mode of the active nanobox. To prove our theory, we consider a similar gold nanoshell with almost identical parameters to the nanobox. More specifically, the gain medium has a refractive index of $1.33 - 0.1437i$, the refractive index of the surrounding medium is 1.33 (therefore $\epsilon_m = 1.77$), and the permittivity of the gold is described by a Drude-Lorentz model [34]. In addition, the core radius is 16 nm and the gold shell thickness is 2 nm. The nonlocal effect of gold is not considered here since it does not influence our results qualitatively [35]. Similar to the first design, we compute the effective permittivities analytically and numerically, and the results are summarized in Fig. 2. Around a wavelength of 789 nm, the complex $\epsilon_c$ is found to be $-3.6$, quite close to $-2\epsilon_m$ (-3.54). The Fröhlich condition is therefore nearly satisfied, so that the first-order surface mode of the active nanoparticle is excited. As a consequence, the nanoshell strongly scatters the incident light and significantly localizes the electromagnetic field around its surface, as can be found from the local field distribution (Fig. 2(c)). We also show in Fig. 2(b) that a negative real permittivity $\epsilon_b = -4.2$ can be attributed to a composite with a filling fraction of 0.093.

To close the discussion, we should mention that $\epsilon_b$ can be tuned by changing the filling fraction $f$, as suggested by Eq. (5). Taking the second design as an example, $f = 0.15$ leads to $\epsilon_b = -3.9$, but $f = 0.25$ gives $\epsilon_b = -3.8$. In addition, it should be stressed that a composite with compensated losses can easily be modified to realize surface plasmon amplification by stimulated emission of radiation (spaser) [11–17]. By increasing the gain coefficient of the inclusive gain medium slightly, it will begin to amplify light or even lase under proper conditions. Therefore, the gain coefficient needed to compensate for the loss of the localized surface plasmon can be set as a threshold for the spaser [12].

In conclusion, an electrostatic theory is developed to design bulk composites with effective negative permittivities with compensated losses. This theory is quite general and accounts for nanoparticles with arbitrary shapes. Moreover, full-wave numerical simulations were used to validate its accuracy. Two different examples were considered to demonstrate the design procedure. It was found that the first-order surface mode of the constitutive nanoparticle should be excited to achieve a negative real-valued $\epsilon_b$. The particle consequently has a zero absorption cross section but a huge scattering cross section, strongly enhancing its localized surface plasmon polariton and the associated surface-enhanced Raman scattering.
References

1. R. Marqués, F. Martín, and M. Sorolla, *Metamaterials with Negative Parameters* (Wiley, 2008).
2. L. Solymar and E. Shamonina, *Waves in Metamaterials* (Oxford University, 2009).
3. *Physics of Negative Refraction and Negative Index Materials*, edited by C. M. Krowne and Y. Zhang (Springer, 2007).
4. D. R. Smith, W. J. Padilla, D. C. Vier, S. C. Nemat-Nasser, and S. Schultz, “Composite Medium with Simultaneously Negative Permeability and Permittivity,” Phys. Rev. Lett. 84, 4184 (2000).
5. J. B. Pendry, “Negative Refraction Makes a Perfect Lens,” Phys. Rev. Lett. 85, 3966 (2000).
6. J. B. Pendry, D. Schurig, and D. R. Smith, “Controlling Electromagnetic Fields,” Science 312, 1780 (2006).
7. U. Leonhardt, “Optical Conformal Mapping,” Science 312, 1777 (2006).
8. D. Schurig, J. J. Mock, B. J. Justice, S. A. Cummer, J. B. Pendry, A. F. Starr, and D. R. Smith, “Metamaterial Electromagnetic Cloak at Microwave Frequencies,” Science 314, 977 (2006).
9. M. Rahm, D. Schurig, D. A. Roberts, S. A. Cummer, D. R. Smith, and J. B. Pendry, “Design of Electromagnetic Cloaks and Concentrators Using Form-invariant Coordinate Transformations of Maxwell’s Equations,” Photonics Nanostruct. Fundam. Appl. 6, 87 (2008).
10. D.-H. Kwon and D. H. Werner, “Transformation Optical Designs for Wave Collimators, Flat Lenses and Right-angle Bends,” New J. Phys. 10, 115023 (2008).
11. D. J. Bergman and M. I. Stockman, “Surface Plasmon Amplification by Stimulated Emission of Radiation: Quantum Generation of Coherent Surface Plasmons in Nanosystems,” Phys. Rev. Lett. 90, 027402 (2003).
12. M. A. Noginov, G. Zhu, M. Bahoura, J. Adegoke, C. E. Small, B. A. Ritzo, V. P. Drachev, and V. M. Shalaev, “Enhancement of Surface Plasmons in an Ag Aggregate by Optical Gain in a Dielectric Medium,” Opt. Lett. 31, 3022 (2006).
13. N. I. Zheludev, S. L. Prosvirnin, N. Papasimakis, and V. A. Fedotov, “Lasing Spaser,” Nat. Photonics 2, 351 (2008).
14. M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Herz, T. Suteewong, and U. Wiesner, “Demonstration of a Spaser-based Nanolaser,” Nature 460, 1110 (2009).
15. R. F. Oulton, V. J. Sorger, T. Zentgraf, R. M. Ma, C. Gladden, L. Dai, G. Bartal, and X. Zhang, “Plasmon Lasers at Deep Subwavelength Scale,” Nature 461, 629 (2009).
16. A. Fang, Th. Koschny, M. Wegener, and C. M. Soukoulis, “Self-consistent Calculation of Metamaterials with Gain,” Phys. Rev. B 79, 241104(R) (2009).
17. M. I. Stockman, “The Spaser as a Nanoscale Quantum Generator and Ultrafast Amplifier,” J. Opt. 12, 024004 (2010).
18. J. A. Gordon and R. W. Ziolkowski, “The Design and Simulated Performance of a Coated Nano-particle Laser,” Opt. Express 15, 2622 (2007).
19. Y. Fu, L. Thylén and H. Ågren, “A Lossless Negative Dielectric Constant from Quantum Dot Exciton Polaritons,” Nano Lett. 8, 1551 (2008).
20. A. Bratkovsky, E. Ponizovskaya, S. Y Wang, P. Holmström, L. Thylén, Y. Fu, and H. Ågren, “A Metal-wire/Quantum-dot Composite Metamaterial with Negative $\epsilon$ and Compensated Optical Loss,” Appl. Phys. Lett. 93, 193106 (2008).
21. E. Ponizovskaya, L. Thylén, A. Bratkovsky, and Y. Fu, “Binary Metal and Semiconductor Quantum Dot Metamaterials with Negative Optical Dielectric Constant and Compensated Loss for Small Volume Waveguides, Modulators and Switches,” Appl. Phys. A 95, 1029 (2009).
22. N. M. Lawandya, “Localized Surface Plasmon Singularities in Amplifying Media,” Appl. Phys. Lett. 85, 5040 (2004).
23. Z. Y Li and Y. Xia, “Metal Nanoparticles with Gain toward Single-Molecule Detection by Surface-Enhanced Raman Scattering,” Nano Lett. 10, 243 (2010).
24. A. L. Aden and M. Kerker, “Scattering of Electromagnetic Waves From Two Concentric Spheres,” J. Appl. Phys. 22, 1242 (1951).
25. C. F. Bohren and D. R. Huffman, Absorption and Scattering of Light by Small Particles (John Wiley & Sons, 1998).
26. J. D. Jackson, Classical Electrodynamics, 3rd Edition, John Wiley & Sons, 2001.
27. V. Yannopapas and A. Moroz, “Negative Refractive Index Metamaterials from Inherently Non-magnetic Materials for Deep Infrared to Terahertz Frequency Ranges,” J. Phys.: Condens. Matter 17, 3717 (2005).
28. M. S. Wheeler, J. S. Aitchison, and M. Mojahedi, “Coated Nonmagnetic Spheres with a Negative Index of Refraction at Infrared Frequencies,” Phys. Rev. B 73, 045105 (2006).
29. H. Fröhlich, Theory of Dielectrics (Oxford, 1949).
30. Handbook of Optical Constants of Solids, edited by E. D. Palik (Academic, 1985).
31. COMSOL, www.comsol.com.
32. D. R. Smith, S. Schultz, P. Markoš, and C. M. Soukoulis, “Determination of Effective Permittivity and Permeability of Metamaterials from Reflection and Transmission Coefficients,” Phys. Rev. B 65, 195104 (2002).
33. C. R. Simovski, “Material Parameters of Metamaterials (A Review),” Optics and Spectroscopy, 107, 726 (2009).
34. A. Vial, A. S. Grimault, D. Macías, D. Barchiesi, and M. L. de la Chapelle, “Improved Analytical Fit of Gold Dispersion: Application to the Modeling of Extinction Spectra with a Finite-Difference Time-Domain Method,” Phys. Rev. B 71, 085416 (2005).

35. J. M. McMahon, S. K. Gray, and G. C. Schatz, “Nonlocal Optical Response of Metal Nanostructures with Arbitrary Shape,” Phys. Rev. Lett. 103, 097403 (2009).
Fig. 1. Spherical semiconductor quantum dots coated with a silver film. (a) The effective permittivity $\varepsilon_c$ of the individual particle, and (b) the effective permittivity $\varepsilon_b$ of the bulk composite. The dotted curves are obtained by full-wave simulations (see text). (c) The first-order surface mode of the individual particle. The field magnitude is color coded. The blue color corresponds to the minimum, while the red color represents the maximum. The polarization of the incident light is along the horizontal direction.

Fig. 2. Same as Fig. 1, except the example is a gold coated gain medium whose refractive index is $1.33 - 0.1437i$. 