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Double-resonance plasmon-driven enhancement of nonlinear optical response in a metamaterial with coated nanoparticles

A. A. Zharov, N. A. Zharova[*1)]

Institute for Physics of Microstructures RAS, 603950 Nizhny Novgorod, Russia

[*] *Institute of Applied Physics RAS, 603950 Nizhny Novgorod, Russia*

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By means of a simple analytical model, we show the possibility of giant double-resonance enhancement of nonlinear cubic optical response of metamaterial containing layered (coated) nanoparticles with nonlinear dielectric core covered by metallic shell. Such nanoparticles support two surface plasmons of dipole type with different eigenfrequencies depending on volume portion of nonlinear dielectric. We demonstrate that giant enhancement of nonlinearity takes place under condition of double resonance when the fundamental frequency of light wave and its third harmonic simultaneously coincide or close to the frequencies of surface plasmons.

1. Introduction. The interaction of light with metallic nanoparticles, nanoparticle arrays and nanostructured metamaterials attracts a great deal of attention in the recent years being the subject of extensive both experimental and theoretical studies [1 – 4]. Mainly, such an interest is caused by plasmonic effects which bode a lot of promising applications in subwavelength microscopy, nanowaveguiding, lithography, biosensorics, etc. Metallic nanoparticles themselves are expected to be the "'bricks"' for creation of novel types of plasmonic metamaterials exhibiting optical properties unreachable for natural media. To date, the nanostructured metamaterials based on two- and three-dimensional lattices of nanoparticles of different designs have been obtained which demonstrate very unusual not only electric but also magnetic resonant response including left-handed behavior in the wide frequency range from midinfrared up to visible or even near-UV bands (see, for example [5 – 11]). Except linear interaction nanostructured metallic metamaterials demonstrate resonant nonlinear both second and third-order response which lead to the second and third harmonic generation respectively [12, 13]. From the microscopic point of view such linear and nonlinear interactions of light with metamaterials arise due to the excitation of plasmon modes of different types in individual particles that leads to the local field increasing and eventually provides a plasmon-assisted enhancement of nonlinear response [14 – 17]. The idea of using layered (or coated) metallo-dielectric nanoparticles and nanoparticle-based metamaterials is the subject of intensive discussions nowadays basically from the viewpoint of creation of mask coatings and electromagnetic invisibility attainment [18 – 20]. However, how it will be shown below, the potential applications of coated nanoparticles are not exhausted by the problem of invisibility cloaks. In this Letter we report that third-order nonlinear susceptibility of a metamaterial with coated nanoparticles can be significantly (in several orders) increased in comparison with nonlinear susceptibility of dielectric in the particle cores because of double resonance interaction of light with coated nanoparticles.

2. Dipole type plasmon eigenmodes in a coated nanoparticle. As a simple model (see Fig.1) we consider a spherical nanoparticle with nonlinear dielectric core of radius a covered by metallic shell with permittivity $\varepsilon_M(\omega)$ and thickness $R-a$, so that full nanoparticle radius is R. The nonlinear permittivity of dielectric core depends on the tension of local electric field $\mathbf{E}$ as $\varepsilon = \varepsilon_D + \chi_D^{(3)}\mathbf{E}^2$. Let this nanoparticle be embedded into linear dielectric host matrix with $\varepsilon = \varepsilon_H$. Assume that all characteristic electromagnetic

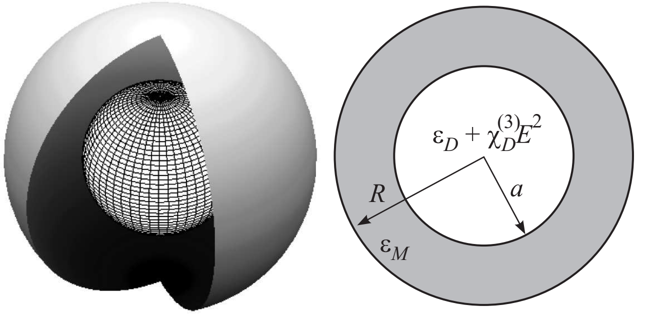

Fig.1. Internal structure of the nanoparticle. Spherical core of radius a made of nonlinear dielectric with permittivity $\varepsilon_D + \chi_D^{(3)}E^2$ is covered by metallic shell with permittivity $\varepsilon_M(\omega)$; the full radius of nanoparticle is R

[1)] e-mail: zhani@appl.sci-nnov.ru

scales such as wavelengths in host matrix and dielectric core, width of skin-layer are notably greater than R that bounds the nanoparticle size R by $10 \div 20$ nm in visible band. In turn, it enables, from one hand, to use the quasi-static description of nanoparticle interaction with light and, from the other hand, to neglect the excitation of higher-order plasmons in nanoparticles, taking into account only plasmons of dipole type. Thus, the first problem to be solved is to find a dipole moment of coated nanoparticle into homogeneous electric field which allows to determine the spectrum of dipole-type plasmon eigenmodes. Within the quasi-static approximation the electric field $\mathbf{E} = -\nabla\Phi$ can be described by potential, Φ , which satisfies Laplas equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\varepsilon(r)\frac{\partial\Phi}{\partial r}\right) + \frac{\varepsilon(r)}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right) = 0 \quad (1)$$

with boundary conditions of continuity of Φ and $\varepsilon\partial\Phi/\partial r$ at $r = a$ and $r = R$, where θ is the polar angle and r is the radial coordinate; $\varepsilon(r)$ is the dielectric permittivity of the coated particle. The azimuth symmetry $(\partial/\partial\phi = 0)$ has been taken into account in Eq.(1). Bearing in mind that nonlinearity of dielectric core is weak enough so that we, first, consider a linear response of the nanoparticle, and then will take nonlinearity into account as a perturbation. The solution of Eq.(1) into dielectric core, metallic shell and outside the particle is represented as follows:

$$\begin{aligned} 0 < r \le a &: \Phi = Ar\cos\theta\ , \\ a < r \le R &: \Phi = \left(Br + C/r^2\right)\cos\theta\ , \\ r > R &: \Phi = \left(E_0 r + P/r^2\right)\cos\theta\ , \end{aligned} \quad (2)$$

where E_0 is the tension of external local electric field and P has a meaning of full dipole moment of nanoparticle. All the constants can be found from the boundary conditions

$$\begin{aligned} &A = 9G(\omega)\varepsilon_H\varepsilon_M(\omega)E_0, \\ &B = 3G(\omega)\varepsilon_H(\varepsilon_D + 2\varepsilon_M(\omega))E_0, \\ &C = a^3G(\omega)\varepsilon_H(\varepsilon_M(\omega) - \varepsilon_D)E_0, \\ &P = R^3G(\omega)[(\varepsilon_H - \varepsilon_M(\omega))(\varepsilon_D + 2\varepsilon_M(\omega)) + \\ &\quad + \rho(\varepsilon_M(\omega) - \varepsilon_D)(2\varepsilon_M(\omega) + \varepsilon_H)]E_0\ , \end{aligned} \quad (3)$$

where $\rho = (a/R)^3$. The zero value of inverse gain factor

$$\begin{aligned} \frac{1}{G(\omega)} &= (\varepsilon_D + 2\varepsilon_M(\omega))(2\varepsilon_H + \varepsilon_M(\omega)) + \\ &+ 2\rho(\varepsilon_M(\omega) - \varepsilon_D)(\varepsilon_H - \varepsilon_M(\omega)) = 0 \end{aligned} \quad (4)$$

determines the eigenfrequencies of dipole-type plasmons supported by coated nanoparticle. Describing $\varepsilon_M(\omega)$ by means of Drude formula $\varepsilon_M(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega - i\nu)}$, where ω_p is the plasma frequency, ν is the electron scattering rate, the Eq.(4) yields (in lossless case $\nu = 0$) the spectrum of these plasmons, which is shown in Fig.2 for different dielectrics of the particle core. Hereinafter

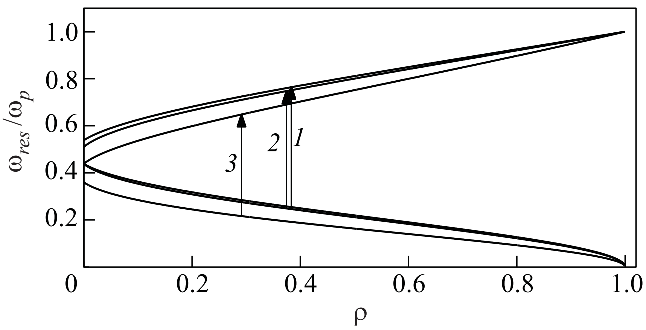

Fig.2. Dipole-type plasmon eigenfrequencies ω_{res} supported by coated particle normalized on plasma frequency of metal ω_p as a function of dielectric filling factor of nanoparticle $\rho = (a/R)^3$ in lossless linear case for three different dielectrics in nanoparticle core: *1* – $BiMnO_3$, $\varepsilon_D = 4.9$, *2* – ZnS, $\varepsilon_D = 5.7$, *3* – GaAs, $\varepsilon_D = 13.4$. Arrows indicate the double resonance conditions for each dielectric core

we suppose for calculations that the host matrix is glass (SiO_2 with dielectric permittivity $\varepsilon_H = 2.1$). One can see that eigenfrequencies of plasmons strongly depend on parameter ρ. It is quite obvious that the frequency of high-frequency plasmon must be equal to the third harmonic of low-frequency one to provide double resonance conditions. It can be implemented only at well-defined values of ρ and ε_D. Figure 3 plots filling factor ρ versus the dielectric permitivity ε_D, for the case when the double resonance conditions are satisfied.

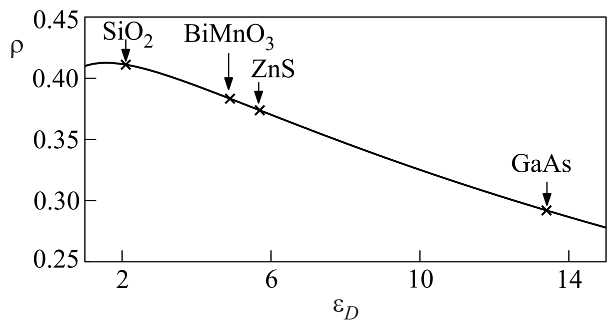

Fig.3. Dependence of filling factor ρ ensuring the fulfilment of double resonance conditions on dielectric permeability ε_D

Under these conditions the amplification of local field in nanoparticle takes place not only at fundamental frequency but also at third harmonic, that leads to the double resonant enhancement of particle dipole moment at third harmonic and results in double resonant increasing of nonlinear third order susceptibility of metamaterial based on the array of such nanoparticles.

3. Nonlinear susceptibility of metamaterial. Let us now consider the metamaterial which is made up by cubic lattice of coated nanoparticles in host. In order to calculate the nonlinear response of metamaterial it is necessary to find the dipole moment of the particle at third harmonic of fundamental frequency that can be done by fixed field approximation keeping the quasi-static approach. For this one needs to calculate the triple frequency perturbation of the surface charge density which is the source of the field of third harmonic. Not very difficult but rather cumbrous calculations lead to the expression for the third harmonic nonlinear polarization density of metamaterial composed of coated particles

$$p_3 = \chi^{(MM)}_{\omega,\omega;\omega} E_0^3 = \\ = -12\pi\rho N R^3 \left(9\varepsilon_M(\omega)G(\omega)\right)^3 \varepsilon_M(3\omega)G(3\omega)\chi^{(3)}E_0^3 \ ,$$

where N is the concentration of nanoparticles. Further we suppose that $NR^3 \ll 1$ so that the local electric field E_0 does not actually differ from the mean macroscopic field (the so-called Lorentz-Lorenz correction [7] is negligibly small). To characterize nonlinear response of metamaterial it is convenient to introduce parameter $\eta = \chi^{(MM)}_{\omega,\omega;\omega}/\chi^{(3)}$ indicating the difference of nonlinear susceptibility of metamaterial from nonlinear susceptibility of dielectric in the core of nanoparticles. The wavelength dependencies of $|\eta(\omega)|$ for metamaterial based on coated nanoparticles with silver shell ($\omega_p \approx$ 8eV, $\nu \approx 1.25 \cdot 10^{-2}$eV [21]) under conditions of double resonance and out of those conditions at different values of ε_D are shown in Fig.4a, b. One can see that the double resonance gives the growth of $|\eta|$ more than in six orders while the single resonance leads to the gain about 4 – 5 orders. If double resonance condition is not met, the main resonance peak (as in Fig.4a) splits into two lower subpeaks (see Fig.4b) with frequency difference defined by the mismatch of the fundamental and third harmonic resonances, i.e. by the different plasmon eigenfrequency shifts at fundamental and third harmonic. The shift of resonance peak towards the red side and decrease of the gain takes place for higher values of nonlinear dielectric permittivity (see Fig.4a). These effects are caused by the increase of the silver shell thickness to provide the double resonance conditions, and also by the growth of Drude energy losses in metal.

Figure 5 shows the dispersion curves for electromagnetic waves in metamaterial with coated nanoparticles. Dashed lines demonstrate the possible phase matching conditions for the waves at first and third harmonics in the case of double resonance enhancement of nonlinearity: $\varepsilon_D = 4.9$, $\rho = 0.3833$.

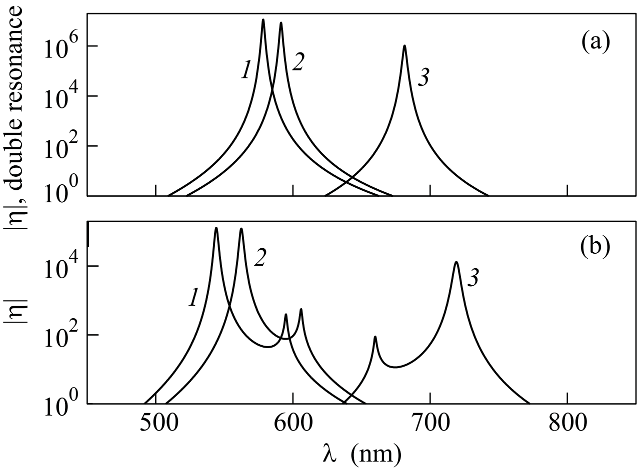

Fig.4. Relative enhancement of nonlinear susceptibility ($|\eta|$) of metamaterial made of the coated nanoparticles with respect to nonlinear susceptibility of the material of dielectric core as a function of vacuum radiation wavelength λ. Upper plot corresponds to the double resonance case. If the conditions of double resonance are not carried out the effect is much weaker (see lower plot). The parameters used for the calculations are: $NR^3 = 0.125$; the values of core dielectric permittivity $\varepsilon_{D(1,2,3)}$ are the same as those given in Fig.2; filling factor values are $\rho_1 = 0.3833$, $\rho_2 = 0.3738$, $\rho_3 = 0.2920$ in upper plot and $\rho_{1,2,3} = 0.333$ in lower plot; $\omega_p \approx$ 8eV, $\nu \approx 1.25 \cdot 10^{-2}$eV that corresponds to silver metal shell [21]

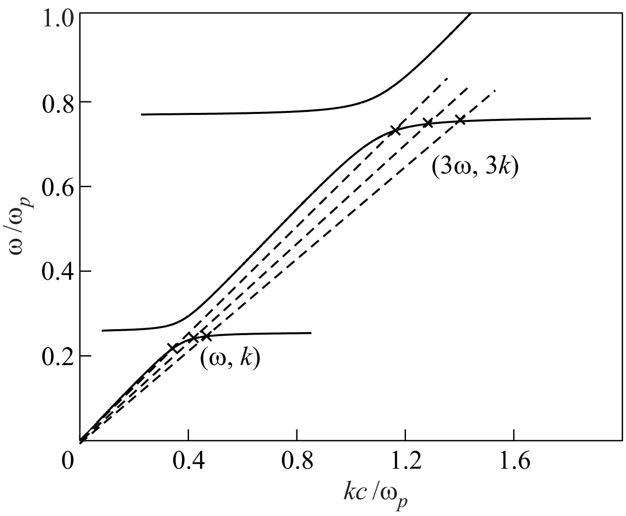

Fig.5. Dispersion curves for electromagnetic waves in metamaterial with coated nanoparticles and possible phase matching conditions for the waves of fundamental frequency and its third harmonic. In calculations the parameters of dielectric core with $\varepsilon_D = 4.9$ ($\rho = 0.3833$) and silver metal shell with $\omega_p \approx 8$ eV, $\nu \approx 0.0125$ eV were used

4. Conclusion. In conclusion, the optical cubic nonlinear susceptibility of metamaterials based upon nonlinear layered metallo-dielectric nanoparticles which leads, in particular, to the third harmonic generation can be significantly (in several orders in comparison with nonlinear susceptibility of nanoparticle dielectric core) amplified due to resonant excitation in nanoparticles of dipole-type plasmons simultaneously both at the fundamental frequency of light and at its third harmonic.

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