Giant enhancement of optical Kerr nonlinearity in random high refractive index nanocomposites near Mie resonances

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The optical Kerr effect of nanocomposites consisting of high refractive index (GaP) spheres is studied by means of three-dimensional finite-difference time-domain (FDTD) simulations at the wavelength of 532 nm. The effective nonlinear refractive index of 0.8 μm thick nanocomposites and metasurfaces is evaluated. It is shown that the optical Kerr nonlinearity of the nanocomposites rises by orders in proximity to Mie resonances and may exceed the second-order refractive index of the bulk material. The nonlinearity enhancement is more pronounced for the metasurfaces. The sign of the effective optical Kerr coefficient is inverted for some range of the sphere sizes above the magnetic dipole resonance.

During the past years, dielectric metasurface technology has been rapidly developed. The dielectric metasurfaces comprising interfaces patterned by high index particles of subwavelength size exhibit exceptional abilities for controlling light [1]. Nowadays, the shape and size of the high index particles can be precisely governed. For example, in Ref. [2], it was demonstrated the fabrication of the metasurface as a monolayer of twisted silicon nanocrescents which exhibited high circular dichroism.

In recent years, nonlinear optical properties of nanostructures containing dielectric high index Mie-type resonant particles have attracted much interest due to their potential applications for designing light sources, optical modulators and novel ultrashort metadevices [3]. Near the resonances, the nanocomposites exhibit inherently large nonlinear response because of optical field localization in the nanoparticles. These particles with high refractive index show enhanced optical nonlinearity due to the field concentration at the optical resonances [4]. Mostly, researchers study elevated third harmonic generation in such nanocomposites. The efficiency of the harmonic generation with near resonant particles is enhanced by two orders of magnitude with respect to the bulk material [5]. Yang et al. [6] measured even higher increase in the third harmonic generation by a Fano-resonant silicon metasurface with the $1.5 \times 10^5$ factor in relation to an unpatterned Si film. However, the effective Kerr nonlinearity of the systems of dielectric Mie-type resonant particles has been left uninvestigated. This work provides the study intended to fill the gap.

Recently, there was proposed a method of restoration of the effective Kerr nonlinearity of nanocomposite media on the base of three-dimensional finite-difference time-domain (FDTD) simulations of light propagation [7]. This technique exploits the phase change induced by the studied sample to the transmitted Gaussian beam. This phase change is computed for different intensities of the Gaussian beam enabling one to estimate the real parts of the nonlinear refractive index of the sample.

In this work, the procedure presented in Ref. [7] is applied to evaluation of the effective nonlinear refractive index of the random nanocomposite containing identical spherical high index inclusions with sizes close to the lowest Mie resonances.

The effective second-order index of refraction is estimated at the light wavelength of 532 nm for the thick nanocomposites and the metasurfaces containing one layer of the spheres. The studied samples represent the random arrangement of the disjoint spheres of the same radius $r$ in space or on plane. The medium surrounding the spheres is air. As depicted in Fig. 1 the modeled Gaussian beam falls perpendicular on the specimen with intensity-dependent index of refraction

$$n = n_0 + n_2 I,$$

where $n_0$ is the linear refractive index, $n_2$ is the second-order nonlinear refractive index, and $I$ is the intensity of the wave. Then, the phase change on the axis of the transmitted beam is calculated in several points in the phase monitor positioned far enough from the sample. The linear fit of the phase change against the beam intensity provides the real part of the second-order index of refraction $n_2$. The nonlinear refractive index computed in the several points permits to estimate its average and standard deviation.

The gallium phosphide (GaP) has a high linear refractive index $n_{0\mu m} = 3.49$ at wavelength $\lambda = 532$ nm [8] and moderately low extinction coefficient (0.0026) which was neglected in this study. Thus, GaP was selected as a material of the inclusions for modelling. The third-order optical susceptibility of the bulk gallium phosphide was measured in the visible range as $\chi^{(3)} \approx 2 \times 10^{-10}$ esu [9] which yields $n_{2\mu m} \approx 6.5 \times 10^{-17}$ m$^2$/W. The values of $n_2$ measured for the infrared wavelengths are one order lower than the first estimate [10, 11]. The first value was applied to the computations. In any case, the values of effective $n_{2\text{eff}}$ calculated in the present work can be scaled for adoption to other magnitude of the second-order index of refraction of the bulk GaP.

Near Mie resonances, the shape of the Gaussian beam transmitted through the specimen is considerably distorted so the size of the FDTD computational domain should be enlarged to obtain the stable results. The size of the computational domain for simulations was $4 \times 4 \times 30 \mu m$ with the space resolution of 5 nm. In the simulations, the distance between the Gaussian beam source and the studied sample was 0.9 μm, the beam radius $w_0$ at the beam waist was 1.1 μm.

At Mie resonances, the small dielectric spheres with the high refractive index display modes with the self-maintaining

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oscillations of the electric and magnetic fields. The first resonance in the dielectric particles with relative permittivity \( \varepsilon > 0 \) is a magnetic dipole resonance. The lowest magnetic dipole and quadrupole Mie resonances for the standalone GaP spheres at \( \lambda = 532 \text{ nm} \) are anticipated for the radii of \( r = 76.1 \) and \( 108.9 \text{ nm} \). The electric quadrupole resonance is expected at \( r = 100.0 \text{ nm} \) \([12]\). This values may be changed significantly in a periodic lattice of the particles (see, e.g. \([13]\)). The present study showed that, at least, the magnetic dipole resonance is not changed appreciably for the randomly positioned spheres.

Table 1 provides the calculated values of the effective intensity-dependent refractive indexes of 0.8 \( \mu \text{m} \) thick samples with different radii of the spheres. The estimates of the effective optical Kerr nonlinearity of random metasurfaces are tabulated in Tab. I. The metasurfaces were monolayers of the particles of the same radius. The thickness of the metasurface was equal to the diameter of the sphere. For comparison, the \( n_2 \) resulting from the effective medium theory \([14]\) are given in Tabs. II. Previously, it was shown that Ref. \([14]\) predicts maximum magnitudes of the effective third-order susceptibility among other effective medium approximations \([7]\). Sometimes at Mie resonances, predominantly in the vicinity of the electric quadrupole resonance, the standard deviation of \( n_{2\text{eff}} \) exceeded its expected value, that cases are omitted in the tables. This occurs because of the large distortions of the Gaussian beam by the resonant particles. For some sizes of inclusions, several realizations of random arrangement was utilized for the FDTD simulations, these cases are shown in the tables as rows with the same particle radii. To validate, the 1.6 \( \mu \text{m} \) thick sample with spheres having the radius of 72 nm was modeled. The results are comparable with the 0.8 \( \mu \text{m} \) thick sample. The wide scatter of the retrieved magnitudes of the nonlinear refractive index of the metasurfaces with different arrangements of the 80 nm radius spheres may be associated with large variations of the particle density. These samples were modeled as 159 nanoparticles lying in the \( 4 \times 4 \mu \text{m} \) area. The interparticle interactions are amplified in the vicinity of the resonance.

It is particularly interesting that in the neighborhood of the optical resonances \( n_{2\text{eff}} \) is several orders larger than would be expected from the nonlinear effective medium theory and even exceeds second-order refractive index of bulk GaP \((6.5 \times 10^{-17} \text{ m}^2/\text{W})\). This phenomenon arises from the giant field concentration inside the high index spheres close to the resonances \([4]\). The optical Kerr nonlinearity of the nanocomposite is larger than that of the bulk material by one or two orders of magnitude near Mie resonances. The similar behavior of the third harmonic generation from silicon nanodisks in proximity to the magnetic dipole resonance was observed in Ref. \([5]\). It should be noted that the second-order refractive index of the metasurface in the range of the sphere sizes just below the magnetic dipole resonance is an order of magnitude higher than that of the thick samples with the same volume fraction of the nanoparticles.

Of special importance is the fact that the sign of the effective second-order refractive index is inverted in some range of the sphere sizes above the magnetic dipole resonance \((76-82 \text{ nm})\). This phenomenon emerges both for the thick specimens and the metasurfaces. In order to validate this, two simulations of the material with \( n_0 \) of GaP and the negative sign of the second-order refractive index were performed (marked with asterisk in Tab. I). In these cases, in the range of particle sizes above the magnetic dipole resonance \( n_{2\text{eff}} \) is positive. It may be related to negative values of effective magnetic permeability \( \mu_{\text{eff}} \) which is observed for the inclusion sizes above the magnetic resonances (see e.g. \([13]\)). Under these circumstances, the specimen serves as a single negative metamaterial. When \( \mu_{\text{eff}} < 0 \) or \( \varepsilon_{\text{eff}} < 0 \) and losses inside the sample are low, the light partially transmits through the specimen by evanescent tunneling. For sphere sizes somewhat above the magnetic dipole resonance, \( n_{0\text{eff}} < 1 \) was found. It is a known fact that the effective refractive index at Mie-type resonance...
Table I. The effective refractive indexes of the thick specimens reconstructed with the FDTD modeling.

| r, nm | n_{0,eff} | n_{2,eff}, m^2/W | n_{3ZPR}, m^2/W |
|-------|-----------|------------------|-----------------|
| 20    | 0.002804  | 1.00334 (5 ± 2)×10^{-21} | 4.514×10^{-21} |
| 30    | 0.04591   | 1.0774 (1.19 ± 0.09)×10^{-10} | 1.065×10^{-19} |
| 40    | 0.009063  | 1.01196 (2.6 ± 0.7)×10^{-20} | 1.537×10^{-20} |
| 50    | 0.02060   | 1.02929 (1.1 ± 0.2)×10^{-19} | 3.847×10^{-20} |
| 60    | 0.03860   | 1.0633 (5.2 ± 0.5)×10^{-19} | 8.409×10^{-20} |
| 70    | 0.06408   | 1.1256 (4.8 ± 0.3)×10^{-18} | 1.743×10^{-19} |
| 80    | 0.07988   | 1.1809 (2.7 ± 0.2)×10^{-17} | 2.499×10^{-19} |
| 90    | 0.09784   | 1.296 (4.8 ± 0.9)×10^{-16} | 3.597×10^{-19} |
| 100   | 0.1056    | 1.363 (3.1 ± 0.9)×10^{-16} | 4.168×10^{-19} |
| 110   | 0.1180    | 1.398 (3 ± 1)×10^{-16} | 5.211×10^{-19} |
| 120   | 0.1268    | 0.591 (1.4 ± 0.3)×10^{-15} | 6.060×10^{-19} |
| 130   | 0.07870   | 0.288 (3.3 ± 0.1)×10^{-16} | 2.437×10^{-19} |
| 140   | 0.1313    | 0.53 (1.44 ± 0.06)×10^{-16} | 6.538×10^{-19} |
| 150   | 0.1405    | 0.46 (6.6 ± 1.6)×10^{-16} | 7.621×10^{-19} |
| 160   | 0.1405    | 0.46 (8.3 ± 0.5)×10^{-16} | 7.621×10^{-19} |
| 170   | 0.1502    | 0.427 (10 ± 0.8)×10^{-16} | 8.897×10^{-19} |
| 180   | 0.1654    | 1.198 (1.1 ± 0.4)×10^{-16} | 1.126×10^{-18} |
| 190   | 0.1927    | 1.31 (1.2 ± 0.4)×10^{-16} | 1.679×10^{-18} |
| 200   | 0.2897    | 0.39 (8.5 ± 2.9)×10^{-16} | 5.657×10^{-18} |
| 210   | 0.3044    | 1.15 (10 ± 0.3)×10^{-15} | 6.611×10^{-18} |
| 220   | 0.1816    | 1.33 (1.1 ± 0.3)×10^{-15} | 1.432×10^{-18} |
| 230   | 0.1951    | 1.446 (9.2 ± 1.9)×10^{-16} | 1.737×10^{-18} |
| 240   | 0.2092    | 1.549 (5.4 ± 0.5)×10^{-16} | 2.110×10^{-18} |
| 250   | 0.2189    | 0.908 (4.3 ± 0.2)×10^{-16} | 2.403×10^{-18} |
| 260   | 0.2442    | 1.698 (2.6 ± 0.3)×10^{-16} | 3.326×10^{-18} |

Table II. The linear n_{0,eff} and second-order n_{2,eff} refractive indexes of random metasurfaces reconstructed with the FDTD modeling and predicted by the effective medium theory [14] n_{3ZPR} for different radii of spheres r. Here f is the volume fraction (concentration) of inclusions, n_{2,eff} is given with the standard deviation. The last row was calculated for 1.6 μm thick sample, otherwise the thickness of the specimen was 0.8 μm.

| r, nm | f | n_{0,eff} | n_{2,eff}, m^2/W | n_{3ZPR}, m^2/W |
|-------|---|-----------|------------------|-----------------|
| 20    | 0.002825 | 1.00387 (6.6 ± 2.8)×10^{-21} | 4.548×10^{-21} |
| 40    | 0.02296  | 1.03542 (1.6 ± 0.3)×10^{-19} | 4.377×10^{-20} |
| 50    | 0.03896  | 1.0647 (6 ± 2)×10^{-19} | 8.512×10^{-20} |
| 60    | 0.06393  | 1.1400 (8 ± 2)×10^{-18} | 1.736×10^{-19} |
| 65    | 0.07938  | 1.218 (5 ± 1)×10^{-17} | 2.473×10^{-19} |
| 70    | 0.09791  | 1.371 (1 ± 0.1)×10^{-15} | 3.602×10^{-19} |
| 70    | 0.09867  | 1.380 (−1.2 ± 0.1)×10^{-15} | −3.655×10^{-19} |
| 72    | 0.1058   | 1.541 (4.3 ± 0.8)×10^{-15} | 4.180×10^{-19} |
| 72    | 0.1055   | 1.515 (3.8 ± 0.5)×10^{-15} | 4.159×10^{-19} |
| 80    | 0.1401   | 0.926 (−2.4 ± 0.7)×10^{-16} | 7.569×10^{-19} |
| 80    | 0.1416   | 0.963 (−5.5 ± 0.9)×10^{-16} | 7.750×10^{-19} |
| 80    | 0.1416   | 0.963 (5.5 ± 1)×10^{-16} | −7.749×10^{-19} |
| 80    | 0.1394   | 0.946 (−4 ± 1)×10^{-16} | 7.482×10^{-19} |
| 85    | 0.1666   | 1.023 (9.8 ± 1.4)×10^{-17} | 1.146×10^{-18} |
| 90    | 0.1927   | 1.115 (1.5 ± 0.1)×10^{-16} | 1.679×10^{-18} |
| 105   | 0.2886   | 0.352 (9 ± 5)×10^{-16} | 5.593×10^{-18} |
| 113   | 0.2499   | 3.194 (1.2 ± 1)×10^{-15} | 3.568×10^{-18} |

may be under unity [15]. Albeit, the sign inversion was not observed in this study for the particle sizes above the quadrupole magnetic resonance. Probably, the range with μ_{eff} < 0 becomes very narrow for the high resonances. It should be emphasized that the only a minor part of the light intensity transmits through the single negative material (see Fig. 2). When the sphere radius is 80 nm the input flux is mostly reflected forming a standing wave before the specimen. Moreover, the substantial portion of the incident energy is scattered by the particles in different directions in the vicinity of the resonance. Whereas for the sphere radii just below magnetic dipole resonance, the nonlinear nanocomposite is much more transparent to light simultaneously having large magnitudes of n_{2,eff}. Thus, this range of particle sizes is preferable for designing nonlinear nanocomposites.

In summary, the real part of the effective Kerr nonlinear refractive index of the random nanocomposites consisting of the high index spheres is estimated. It is shown that the nanostructure second-order refractive index near Mie resonances exceeds that of the bulk material by one or two orders of magnitude.

Figure 2. Distributions of the time-average electric energy density within the cross section of the initial part of the computational domain along the Gaussian beam axis for different radii of the spheres: 65 nm, 70 nm, 80 nm (from top to bottom). The beam is incident on a monolayer of the GaP spheres.
magnitude. The metasurfaces display the larger Kerr nonlinearity enhancement in proximity to Mie resonances than the thick samples. The sign of the second-order refractive index is inverted for the nanocomposite with the sphere diameters slightly higher than the size of the magnetic dipole resonance. The results were obtained with the use of IACP FEB RAS Shared Resource Center “Far Eastern Computing Resource” equipment (https://www.cc.dvo.ru).

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