Theory of nondegenerate nonlinear optical susceptibilities of graded composites with high-volume fractions

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We present a theory for the effective nondegenerate third-order nonlinear optical susceptibility (NDTNOS) of composite media in which the graded metallic particles with weak nonlinearity and the linear dielectric grains are randomly distributed. In combination with an effective medium approximation, the recently established nonlinear differential effective dipole approximation (NDEDA), which is valid for the degenerate third-order optical nonlinearity of the composites in the dilute limit, is generalized to deal with the effective NDTNOS of graded composites of high-volume fractions. Numerical results show that for high-volume fractions, the presence of gradation makes the effective NDTNOS enhanced, but the linear optical absorption reduced, thus, yielding an attractive figure of merit. In addition, by using NDEDA and Maxwell-Garnett approximation, we study the effective NDTNOS of the graded composite media with the Hashin-Shtrikman microgeometry. The nondegenerate optical nonlinearity enhancement is found to be sensitive to the composite topology.

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Nonlinear optical properties of granular composite materials have been the subject of extensive research because of their potential applications in physics and engineering [1–3]. A large optical nonlinearity enhancement was experimentally observed in a broad variety of artificial materials, such as the multilayer of titanium dioxide and conjugated polymer [4], and the metal-dielectric nanocomposite [5]. On the other hand, a number of theoretical works have been devoted to achieving a large enhancement of nonlinear optical susceptibilities by taking into account the local-field effect and the percolation effect [6,7].

Recently, graded materials have attracted much interest in various engineering applications [8]. For treating the effective dielectric response of composites containing graded particles, we proposed a nonlinear differential effective dipole approximation (NDEDA) [9], valid in the dilute limit.

Generally, the effective optical nonlinear susceptibility reported in previous works is a degenerate component, namely, $\chi_e(\omega)\equiv\chi_e(\omega:-\omega,\omega,\omega)$. However, in the nondegenerate four-wave mixing, one should impose the two pump fields with ω_1 of high intensity to generate the desired nonlinearity, while the probe field at ω_2 of lower intensity is measured. For instance, the differential absorption spectra [10] are related to the effective nondegenerate third-order nonlinear optical susceptibility (NDTNOS) $\chi_e(\omega_2)\equiv\chi_e(\omega_2:-\omega_1,\omega_1,\omega_2)$ defined as

$$\chi_e(\omega_2)|\mathbf{E}_{0,\omega_1}|^2\mathbf{E}_{0,\omega_2}^2=\frac{1}{V}\int\chi_i|\mathbf{E}_{\mathrm{loc},\omega_1}|^2\mathbf{E}_{\mathrm{loc},\omega_2}^2\mathrm{d}V,$$

where χ_i stands for the NDTNOS of the component i, and $\mathbf{E}_{\mathrm{loc},\omega}$ represents the linear local field when the external field of ω ($\mathbf{E}_{0,\omega}$) is applied. This susceptibility is qualitatively different from the degenerate one in that it intrinsically involves two different frequencies. In this Brief Report, we shall generalize the NDEDA [9], which is valid for the degenerate third-order nonlinear optical susceptibility of graded composites in the dilute limit, to treat the effective NDTNOS of composite media containing spherical graded particles with high volume factions. For this purpose, the Bruggeman effective medium approximation (EMA) will be adopted. Furthermore, we also apply the NDEDA to study the effective NDTNOS of the composite with H-S microstructure.

Let us consider a two-phase composite material in which the graded metallic particles with volume fraction p, and the dielectric grains of the dielectric constant $\epsilon_2(\omega)$ with $1-p$ are randomly distributed. In this system, the graded particles with the same radius a are assumed to possess the weakly nonlinear displacement ($\mathbf{D}$)-field ($\mathbf{E}$) relation of the form, $\mathbf{D}_{1,\omega_2}=\epsilon(r,\omega_2)\mathbf{E}_{1,\omega_2}+\chi(r,\omega_2)|\mathbf{E}_{1,\omega_1}|^2\mathbf{E}_{1,\omega_2}$, where $\epsilon(r,\omega)$ and $\chi(r,\omega)$, respectively, stand for the linear dielectric constant and the NDTNOS of graded particles at the frequency ω. It is worth noting that both $\epsilon(r,\omega)$ and $\chi(r,\omega)$ are radial functions.

Within the quasistatic approximation, the whole inhomogeneous composite behaves as an effective homogeneous one with the effective linear dielectric constant $\epsilon_e(\omega_2)$ and NDTNOS $\chi_e(\omega_2)$, given by

$$\langle\mathbf{D}_{\omega_2}\rangle=\epsilon_e(\omega_2)\mathbf{E}_{0,\omega_2}+\chi_e(\omega_2)|\mathbf{E}_{0,\omega_1}|^2\mathbf{E}_{0,\omega_2}, \tag{1}$$

where $\langle\cdots\rangle$ denotes the spatial average.

To obtain $\epsilon_e(\omega)$ and $\chi_e(\omega)$, we consider the composites in which both the nonlinear graded spherical inclusions and the dielectric grains are embedded in the host medium with undetermined linear dielectric constant $\epsilon_e(\omega)$. The equivalent dielectric constant $\overline{\epsilon}(r,\omega)$ of the graded particles at radius r receives the form [9]

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$$\frac{\mathrm{d}\overline{\epsilon}(r,\omega)}{\mathrm{d}r} = \frac{[\epsilon(r,\omega) - \overline{\epsilon}(r,\omega)][\overline{\epsilon}(r,\omega) + 2\epsilon(r,\omega)]}{r\epsilon(r,\omega)}. \quad (2)$$

Then, the effective linear dielectric constant $\epsilon_e(\omega)$ of the whole system is self-consistently given by the Bruggeman EMA:

$$p\frac{\overline{\epsilon}(a,\omega) - \epsilon_e(\omega)}{\overline{\epsilon}(a,\omega) + 2\epsilon_e(\omega)} + (1-p)\frac{\epsilon_2(\omega) - \epsilon_e(\omega)}{\epsilon_2(\omega) + 2\epsilon_e(\omega)} = 0. \quad (3)$$

For the equivalent NDTNOS $\overline{\chi}(r,\omega_2)$ of the graded particles, we have

$$\frac{\mathrm{d}\overline{\chi}(r,\omega_2)}{\mathrm{d}r} = \overline{\chi}(r,\omega_2)\left[\sum_{n=1}^{2}\frac{n\mathrm{d}\overline{\epsilon}(r,\omega_n)/\mathrm{d}r}{\overline{\epsilon}(r,\omega_n) + 2\epsilon_e(\omega_n)} + \left(\frac{\mathrm{d}\overline{\epsilon}(r,\omega_1)/\mathrm{d}r}{\overline{\epsilon}(r,\omega_1) + 2\epsilon_e(\omega_1)}\right)^*\right] + \frac{\overline{\chi}(r,\omega_2)}{r}[y(r,\omega_1) + y^*(r,\omega_1) + 2y(r,\omega_2) - 3] + \frac{3\chi(r,\omega_2)G}{5r}, \quad (4)$$

where

$$y(\omega) = 2\frac{[\epsilon(r,\omega) - \epsilon_e(\omega)][\overline{\epsilon}(r,\omega) - \epsilon(r,\omega)]}{\epsilon(r,\omega)[\overline{\epsilon}(r,\omega) + 2\epsilon_e(\omega)]},$$

and

$$G = 5|B(\omega_1)|^2[B^2(\omega_2) + 2C^2(\omega_2)] + 4B^*(\omega_1)C(\omega_1)C(\omega_2)[2B(\omega_2) + C(\omega_2)] + 8B(\omega_2)C^*(\omega_1)C(\omega_2)[B(\omega_1) + C(\omega_1)] + 4C^*(\omega_1)C^2(\omega_2)[B(\omega_1) + 6C(\omega_1)] + 10B^2(\omega_2)|C(\omega_1)|^2,$$

with $B(\omega)[C(\omega)] = [\overline{\epsilon}(r,\omega) \pm 2\epsilon(r,\omega)]/[3\epsilon(r,\omega)]$.

Next, we resort to the spectral represent theory [11] and adopt the decoupling approximation to investigate the effective NDTNOS of the composites. That is,

$$\chi_e(\omega_2) = p\overline{\chi}(a,\omega_2)\int_0^1 \left|\frac{s(\omega_1)}{s(\omega_1) - x}\right|^2 \times m(x)\mathrm{d}x \cdot \int_0^1 \left(\frac{s(\omega_2)}{s(\omega_2) - x}\right)^2 m(x)\mathrm{d}x, \quad (5)$$

where $s(\omega) \equiv \epsilon_e(\omega)/[\epsilon_e(\omega) - \overline{\epsilon}(\omega)]$ and $m(x)$ is the spectral density function given in Ref. [11]. Here we mention that the decoupling procedure will be accurate when the local field is nearly uniform and less accurate when the field fluctuations are large, as in a random composite near the percolation threshold.

As a model system, we consider the graded spherical particles to be a Drude-like metal, which has a linear dielectric constant of the form [9]

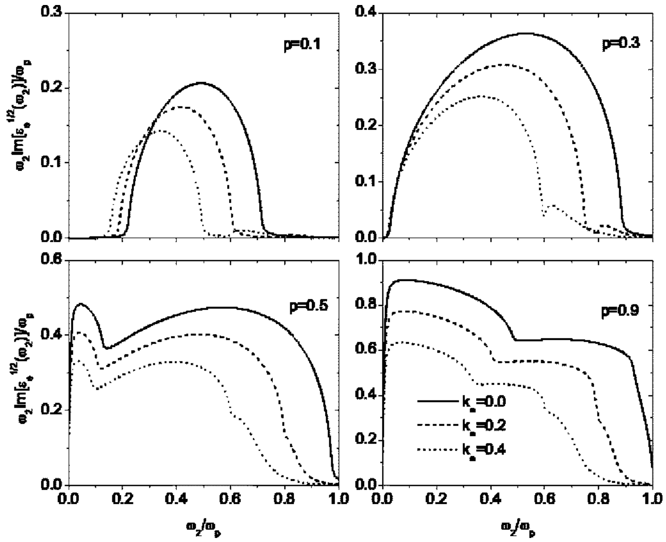

FIG. 1. The linear optical absorption $\omega_2\,\mathrm{Im}[\sqrt{\epsilon_e(\omega_2)}]/\omega_p$ vs ω_2/ω_p, for various k_ω and p.

$$\epsilon(r,\omega) = 1 - \frac{\omega_p^2(r)}{\omega(\omega + \mathrm{i}\gamma)}, \quad r \leqslant a, \quad (6)$$

where γ is the relaxation rate and $\omega_p(r)$ represents the plasma-frequency gradation profile. For numerical calculations, $\omega_p(r)$ is assumed to have the form $\omega_p(r) = \omega_p(1 - k_\omega r/a)$ [9]. Furthermore, to highlight the composite effect, we set $\chi(r,\omega) \equiv \chi_1$ to be independent of both r and ω.

Figure 1 displays the linear optical absorption coefficient $\alpha \sim \omega_2/\omega_p\,\mathrm{Im}[\sqrt{\epsilon_e(\omega_2)}]$ versus the normalized frequency ω_2/ω_p, for $\omega_1 = \omega_p/\sqrt{1+2\epsilon_2}$. Due to the electromagnetic interaction between the individual grains, there are surface plasmon resonant bands in the whole frequency region $0 < \omega < \omega_p$. Moreover, at high-volume fraction, which is larger than the percolation threshold $p_c = 1/3$, a Drude peak appears, characterized by a fast increase of linear absorption near $\omega \sim 0$. To one's interest, when a plasma-frequency gradation profile is taken into account, the surface resonant bands are split into two parts: one is due to randomness; the other (within the high-frequency region) results from the plasmon-frequency gradation. In particular, at high-volume fraction, the presence of gradation leads to a significant decrease in the magnitude of the optical absorption band.

In Fig. 2, we study the enhancement of the effective NDTNOS $|\chi_e(\omega_2)/\chi_1|$. Owing to gradation, the resonant bands due to randomness are caused to be redshifted, while the other enhancement bands are induced to appear in the high-frequency region. The latter enhancement can be well understood if we regard the graded particles as a limit of multishells [12]. Furthermore, for high-volume fraction, the enhancement of the effective NDTNOS for graded composites is larger than the one for the nongraded composites. Therefore, for high p, by choosing an appropriate gradation profile, it is possible to achieve a more prominent enhancement of the effective NDTNOS accompanied with a small linear optical absorption.

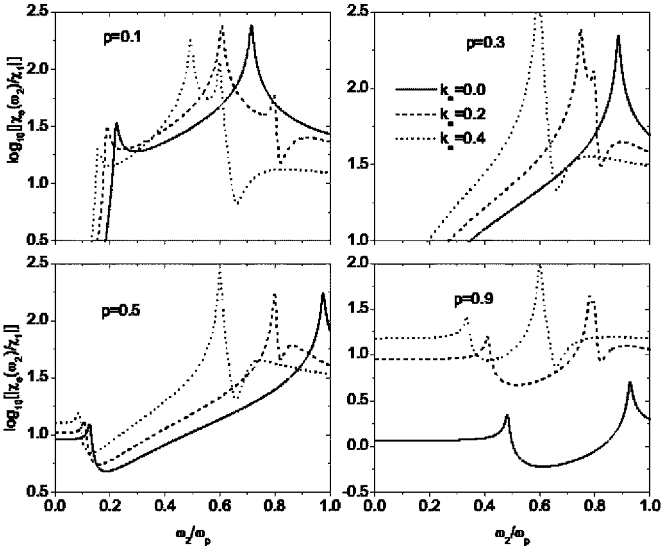

FIG. 2. Same as Fig. 1, but for the effective NDTNOS $|\chi_e(\omega_2)/\chi_1|$.

For practical applications, the most useful parameter is the figure of merit (FOM), defined as $|\chi_e(\omega_2)/\chi_1|/\alpha$ (see Fig. 3). At large volume fraction, the FOM for the graded composites is apparently larger than the one for the nongraded composites. This could not be observed in our previous work [9] where the NDEDA is valid in the dilute limit.

In what follows, we shall derive the NDEDA for the Hashin-Shtrikman (HS) microgeometry. Now, we have a two-phase composite consisting of entirely coated spheres with a nonlinear graded core of dielectric properties $\epsilon(r,\omega)$ and $\chi(r,\omega)$ and a concentric shell of $\epsilon_2(\omega)$. For this kind of microstructure, the equivalent linear dielectric constant $\overline{\epsilon}(r,\omega)$ of graded inclusions can still be described by Eq. (2). However, because the nonlinear graded particles (cores) are always surrounded by the host medium of the dielectric constant $\epsilon_2(\omega)$, the corresponding equivalent NDTNOS can be obtained from Eq. (4) with $\epsilon_e(\omega)$ being replaced by $\epsilon_2(\omega)$.

Once $\overline{\epsilon}(r,\omega)$ and $\overline{\chi}(r,\omega)$ are calculated, the effective linear dielectric constant of the graded composites with the HS microgeometry is described by Maxwell-Garnett approximation (MGA),

$$\frac{\epsilon_e(\omega_2)}{\epsilon_2(\omega_2)} = 1 + \frac{3p[\overline{\epsilon}(a,\omega_2) - \epsilon_2(\omega)]}{(1-p)\overline{\epsilon}(a,\omega_2) + (2+p)\epsilon_2(\omega_2)}. \tag{7}$$

The effective NDTNOS for H-S microgeometry is given by

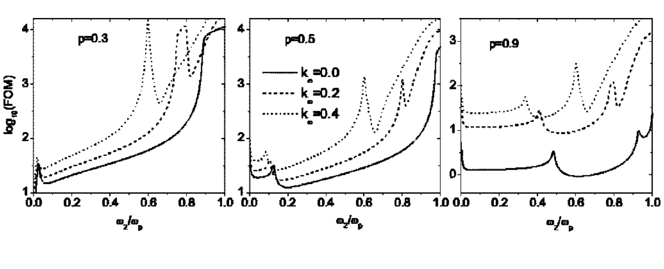

FIG. 3. Same as Fig. 1, but for the FOM.

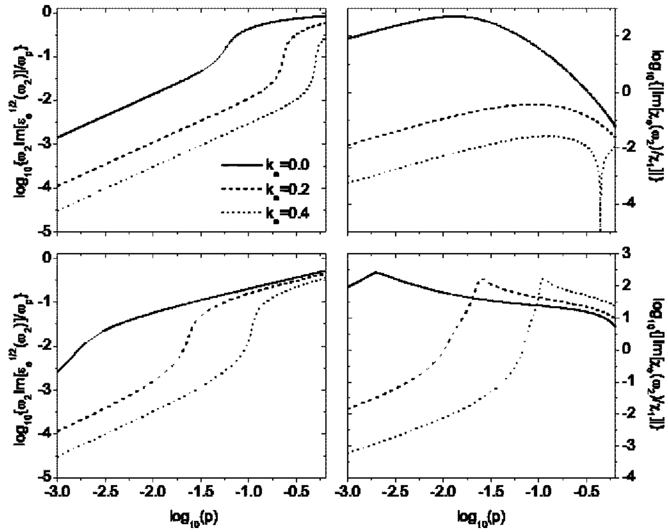

FIG. 4. The nonlinear optical absorption as a function of p for various k_ω. The results of both the NDEDA accompanied with the MGA (left panels) and the EMA (right panels) are shown.

$$\chi_e(\omega_2) = p\overline{\chi}(a,\omega_2)\left|\frac{3\epsilon_2(\omega_1)}{(1-p)\overline{\epsilon}(a,\omega_1) + (2+p)\epsilon_2(\omega_1)}\right|^2 \cdot\left(\frac{3\epsilon_2(\omega_2)}{(1-p)\overline{\epsilon}(a,\omega_2) + (2+p)\epsilon_2(\omega_2)}\right)^2. \tag{8}$$

In Fig. 4, we display the linear absorption $\alpha \sim \omega_2/\omega_p \operatorname{Im}[\sqrt{\epsilon_e(\omega_2)}]$ and nonlinear absorption $\beta \sim |\operatorname{Im}[\chi_e(\omega_2)/\chi_1]|$ as a function of p. Both the linear and nonlinear absorption are in direct proportion to p at low-volume fraction, predicted from either the NDEDA accompanied with the EMA or the NDEDA accompanied with the MGA. Then, the linear absorption deviates from the linear dependence on p and undergoes a sharp increase at a certain high-volume fraction, dependent on the gradient k_ω. At small gradients, after the linear dependence, the nonlinear absorption for the NDEDA accompanied with the MGA goes through a maximum and then decreases monotonically with p. For large gradient $k_\omega=0.4$, a sharp valley appears at $p \approx 0.44$, and $\operatorname{Im}[\chi_e(\omega_2)/\chi_1]$ crossovers from the negative value to positive one. However, for the NDEDA accompanied with the EMA, broad nonlinear absorption bands are observed again. Moreover, for large gradient $k_\omega=0.4$, a linear enhancement of nonlinear absorption is found for $0<p<3\times10^{-2}$. At volume fraction $3\times10^{-2}<p<0.112$, the degree of enhancement is higher. After that, the monotonic decrease of nonlinear absorption with p comes to appear due to the formation of large clusters. All these properties are in qualitative agreement with the experiment report [10]. In order to compare with experiment results quantitatively, we should apply the Shalaev-Sarychev theory [1,2] by taking into account the mutual interaction effects exactly. On the other hand, because graded films can be fabricated easily, we suggest experiments be done to examine the gradation effect in the graded metallic films [13].

In conclusion, we have developed the NDEDA accompanied with the EMA for calculating the NDTNOS of a graded composite in which the nonlinear graded metallic particles and the linear dielectric grains are randomly distributed. At high-volume fraction, the presence of gradation was found to be helpful to achieve a large enhancement of the NDTNOS and FOM. The effect of composite topology has also been studied by using the NDEDA accompanied with the MGA.

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