Third-Order Nonlinear Optical Susceptibilities of Colloidal Crystals

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On the basis of the Ewald–Kornfeld formulation, we studied the effective third-order nonlinear optical susceptibilities for nondegenerate four-wave mixing and third-harmonic generation in colloidal crystals, which are made of graded metallodielectric nanoparticles suspended in a host fluid. Theoretical results show that both an enhancement and a red shift of the optical nonlinearity in such colloidal crystals appear due to the effects of local fields and lattice structure. Furthermore, the presence of the dielectric gradation is helpful to achieve large enhancement of nonlinearity at low frequencies.

I. Introduction

Nonlinear optical materials have received much attention, especially those with large nonlinear susceptibilities. Usually, two ways are used to achieve enhanced nonlinearities. One is to find materials with a large intrinsic nonlinear susceptibility, and the other is to fabricate composite materials with an effective nonlinear response exceeding that of each component inside. For the latter, the origin of the enhanced nonlinear susceptibility may be due to the effect of enhanced local fields. For instance, a large nonlinearity enhancement was experimentally reported for a subwavelength multilayer of titanium dioxide and conjugated polymer.

Colloidal crystals are extensively studied in nanomaterial engineering; for examples, see refs 13–17. Schuth et al. have developed a deft colloidal templating process which allows simple cubic crystals to be formed from more readily available complex precursors. Also, by using the nanotechnology, such as methods based on capillary forces and dielectrophoresis, it is possible to fabricate various kinds of colloidal crystals. They can exhibit body-centered tetragonal (bct), body-centered cubic (bcc), and face-centered cubic (fcc) structures, depending on the lattice constants and hence the volume fraction of colloidal particles. These structures can be investigated by using static and dynamic light scattering techniques.

In this paper, we shall theoretically investigate the effective third-order nonlinear optical susceptibilities for nondegenerate four-wave mixing (NDFWM) and third-harmonic generation (THG) in colloidal crystals, which are made of graded metallodielectric nanoparticles (specifically, a graded metallic core plus a dielectric shell) suspended in a host fluid.

NDFWM is a process of the interaction between four waves, namely, two counterpropagating pump beams and one probe beam interact in a nonlinear medium to generate a signal beam that travels backward with respect to the probe beam. This process can be applied in the phase conjugate mirrors, wave restoration, real-time holography, and so on. By using the laser imposing or other relevant techniques, two pump fields (incident fields) with frequency ω1 of high intensity are incident on the nonlinear medium to generate the desired nonlinearity. Meanwhile, the probe field with ω2 of lower intensity is measured. When ω2 = ω1, it becomes the degenerate four-wave mixing, whose nonlinear susceptibility is exactly the same as the usual effective third-order nonlinearity susceptibility χ(3)(ω2), namely

\[ \chi^{(3)}(\omega_2) = \langle \gamma(\omega_2)F(\omega_2)^2|F(\omega_2)|^2 \rangle \]  

(1)

where F stands for the local field enhancement factor, γ(ω2) is the intrinsic third-order nonlinear optical susceptibility, and \( \langle \cdots \rangle \) means the volume average of \( \cdots \). For the present effective NDFWM susceptibility \( \chi_0(\omega_2) \), we obtain the general form such that

\[ \chi_0(\omega_2) = \langle \gamma(\omega_2)F(\omega_2)^2|F(\omega_1)|^2 \rangle \]  

(2)

Thus, the intrinsic third-order nonlinear optical susceptibility \( \gamma(\omega_2) \) plays a crucial role in the effective NDFWM susceptibility, as given by eq 2. Both \( F(\omega_2)^2 \) and \( |F(\omega_1)|^2 \) can be expressed in the spectral representation.

On the other hand, THG is a process of a laser beam incident upon a crystal with the generation of another wave at thrice the optical frequency in the medium. THG can be visualized by considering the interaction in terms of the exchange of photons.
between the various frequencies of the field. According to this mechanism, three photons of frequency \( \omega \) are destroyed, and a photon of frequency \( 3\omega \) is simultaneously created. Thus, the incident wave generates a nonlinear polarization which oscillates with thrice the fundamental frequency. According to Maxwell’s equations, this nonlinear polarization radiates an electromagnetic field with triple frequency. In this case, THG is caused by the intrinsic third-order nonlinear susceptibility, while for the THG induced from second-harmonic generation (SHG), the process is composed of the SHG (two photons absorption) and sum frequency generation. Thus, as far as THG is concerned, two effects will be taken into account in this work. One results from the intrinsic THG susceptibility of the nonlinear graded particles, and the other is the induced THG due to the presence of SHG of graded particles (i.e., the fundamental frequency is doubled due to a nonzero SHG susceptibility, and then the doubled and the fundamental frequencies are added in a sum-frequency process). Regarding SHG, we would like to mention more research background herein. Both theoretical and experimental reports suggested that spherical particles may exhibit a rather unexpected and nontrivial behavior. SHG, due to the broken inversion symmetry at particle surfaces, despite their central symmetry, which seemingly prohibits second-order nonlinear effects. In colloidal suspensions, the SHG response for centrosymmetrical particles was experimentally reported. Thus, the SHG from the centrosymmetrical structure has received extensive attention (see, for example, refs 26 and 27). The SHG under our consideration can just been seen to appear due to the broken inversion symmetry at particle surfaces.

This paper is organized as follows. In section II, we describe the formalism for investigating the effective third-order nonlinear optical susceptibility for NDFWM and THG. In section IV, numerical results are presented under different conditions. This paper ends with a conclusion in section IV.

II. Formalism

First, we consider a nonlinear composite system, in which identical graded metallic spherical particles with radius \( a \) are randomly suspended in a host fluid with (isotropic) dielectric constant \( \varepsilon_2 \). The metallic particle is coated with a dielectric shell of thickness \( d \) and the same dielectric constant \( \varepsilon_2 \), so that multipolar interaction between the metallic particles can be small enough to be neglected. This is actually doable in experiments, such as by choosing silicone oil with a dielectric constant of 2.25 as a host fluid and glass with a dielectric constant of 2.25 as the shells. In so doing, we might focus on the lattice (local field) effect in the presence of gradation. The local constitutive relation between the displacement \( \mathbf{D}(r) \) and the electric field \( \mathbf{E}(r) \) inside of the graded metallic particle (core) is given by

\[
\mathbf{D}(r) = \sum_{i=x}^{z} \varepsilon_i(r) \mathbf{E}(r) + \sum_{j,k=x}^{z} d_{jk}(r) \mathbf{E}_j(r) \mathbf{E}_k(r) + \sum_{j,k,l=x}^{z} \chi_{ijkl}(r) \mathbf{E}_j(r) \mathbf{E}_k(r) \mathbf{E}_l(r) \quad (3)
\]

where \( i = x, y, z \), \( D_i(r) \) and \( E_i(r) \) are the \( i \)th components of \( \mathbf{D}(r) \) and \( \mathbf{E}(r) \), \( d_{jk} \) is the component of the second-order (third-order) nonlinear susceptibility tensor of the graded spherical
nanoparticles, and \( \epsilon_{ij}(r) \) is the linear dielectric constant of the nanoparticle, which is assumed to be isotropic, \( \epsilon_i(r) = \epsilon(r) \), in this work so that we might focus on nonlinear optical responses. Here, \( \epsilon_1(r), d_{ijkl}(r), \) and \( \chi_{ijkl}(r) \) are mathematically the gradation profiles as a function of position \( r \). Our analysis will focus on the weak nonlinearity condition. Namely, the nonlinear part is assumed to be smaller when compared to the linear part. Then, we will resort to the quasi-static approximation.

Colloidal crystals which are made of graded metallodielectric nanoparticles can exhibit bct, bcc, and fcc structures, depending on the lattice constants and the volume fraction of colloidal particles. When an external electric field \( E_0 \) is applied along the \( x \) axis, the induced dipole moment \( p \) is perpendicular to the uniaxial anisotropic axis (\( z \) axis). Below, we apply the Ewald–Korneld model to compute the local electric field of a tetragonal unit cell. It has a basis of two colloidal nanoparticles, each of which is fixed with an induced point dipole at its center. One of the two nanoparticles is located at a corner, and the other is at the body center of the cell, which is shown in Figure 1. As the uniaxial anisotropic axis is directed along the \( z \) axis, the lattice constants can be denoted by \( C_1(=C_2) = lq^{-1/2} \) along the \( x \) (\( y \)) axis and \( C_3 = lq \) along the \( z \) axis. In general, for a colloidal crystal, the individual colloidal nanoparticle should be touching. The lattice parameters satisfy the geometric constraint that \( C_1^2 + C_2^2 + C_3^2 = 16(a + d)^2 \) when we take into account the dielectric surface layer with thickness \( d \) on the graded metallic core (\( a \) is the radius of the metallic core). Then, the degree of anisotropy of the periodic lattice is measured by how \( q \) deviates from unity. In particular, \( q = 0.87358, 1.0, \) and \( 2^{1/3} \) represent the bct, bcc, and fcc lattices, respectively. Here, we assume that the colloidal particles are packed closely, which can be a good approximation with most realistic colloidal systems. Actually, a colloidal crystal without the particles touching can also be made if the colloidal particles are charged or stabilized by the electrostatic force. Below, we investigate the colloidal crystals with particles touching, and the relation between \( q \) and \( \rho \) (the volume fraction of the metallic component) is given by

\[
\rho = \frac{\pi}{24t^3} \sqrt{\left(\frac{q^3 + 2}{q}\right)^{3/2}} \tag{4}\]

Here, \( t \) denotes a thickness parameter, \( t = (a + d)/a > 1 \). Considering the field contribution from all of the other particles in the lattice, the local field \( E_L \) at the lattice point \( \tau = 0 \) can be given by

\[
E_L = \rho \sum_{j=1}^{3} \sum_{R=0}^{2} \left[ -B(R) + x_j q^2 C(R) \right] - \frac{4\pi p}{V_c} \sum_{G=0}^{G_c} \Theta(G) \frac{G^2}{G^2} \exp\left(-\frac{G^2}{4\eta^2}\right) + \frac{4\eta^3}{3\sqrt{\pi}} \tag{5}\]

where \( p \) is the induced dipole moment, \( x_j = l - (j - 1)/2 \), \( R_j = |\mathbf{R} - [(j - 1)/2]a\mathbf{x} + b\mathbf{y} + c\mathbf{z}| \), and \( \Theta(G) = 1 + \exp[i(u +
In eq 5, $B$ and $C$ are two coefficients given in ref 28. $B(r) = \text{erfc}(\eta r)/r^3 + (2\eta/(\pi^{1/2}r)) \exp(-\eta^2r^2)$, and $C(r) = 3\text{erfc}(\eta r)/r^3 + [4\eta^2/(\pi^{1/2}r^2) + 6\eta/(\pi^{1/2}r^2)] \exp(-\eta^2r^2)$, where \text{erfc}(\eta r) is the complementary error function and $\eta$ is an adjustable parameter making the summation converge rapidly.\textsuperscript{9} $G$ denotes the reciprocal lattice vector of $R$. Now, we define a local field factor in the transverse-field case.

$$G$$

To proceed, the dielectric constant $\epsilon_1(r)$ of the graded metallic particle at frequency $\omega$ is expressed in the Drude form as

$$\epsilon_1(r, \omega) = 1 - \frac{\omega_p(r)^2}{\omega(\omega + \gamma)} \quad r \leq a \quad (7)$$

where $\omega_p(r)$ denotes the plasma frequency gradation profile varying with the function of $r$ and $I = (-1)^{1/2}$ and $\gamma$ represents the relaxation rate. For numerical calculations, we take the plasma frequency gradation profile as\textsuperscript{30}

$$\omega_p(r) = \omega_p(0)(1 - C_\alpha r) \quad (8)$$

where $C_\alpha$ is the gradation parameter, which can be tuned to get desired gradation profiles. One possible way to achieve such gratation is to fabricate a graded metallic core by using different noble metals as different layers inside of the core. To obtain

\begin{align*}
\nu + \omega/\pi]. & \\
\text{In eq 5, } B & \text{ and } C \text{ are two coefficients given in ref } 28. \\
B(r) = \text{erfc}(\eta r)/r^3 + (2\eta/(\pi^{1/2}r)) \exp(-\eta^2r^2), \text{ and } C(r) = 3\text{erfc}(\eta r)/r^3 + [4\eta^2/(\pi^{1/2}r^2) + 6\eta/(\pi^{1/2}r^2)] \exp(-\eta^2r^2), \text{ where } \text{erfc}(\eta r) \text{ is the complementary error function and } \eta \text{ is an adjustable parameter making the summation converge rapidly.}\textsuperscript{9} \\
G & \text{ denotes the reciprocal lattice vector of } R. \text{ Now, we define a local field factor in the transverse-field case }
\end{align*}
the effective dielectric constant $\varepsilon_e$ of the colloidal crystal, we resort to the anisotropic Maxwell–Garnett formula\(^31\)

$$\frac{\varepsilon_e - \varepsilon_2}{\alpha \varepsilon_e + (3 - \alpha) \varepsilon_2} = \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2 \varepsilon_2}$$

(9)

where $\rho$ is the volume fraction of the metallic component and the equivalent dielectric constant $\varepsilon_1 \equiv \varepsilon_1(r = a)$ for the graded metallic core can be obtained by solving $d\tilde{\varepsilon}_1(r)/dr = [\varepsilon_1(r) - \varepsilon_1(r)][\varepsilon_1(r) + 2\varepsilon_1(r)]/r\varepsilon_1(r)$\(^32,33\) as long as the gradation profile $\varepsilon_1(r)$ [or $\varepsilon_1(r, \omega)$] is given. In eq 9, the local field factor $\alpha$ can be obtained by solving eqs 5 and 6.

According to eq 2, the effective NDFWM susceptibility $\chi_e(\omega_2)$ for the system of our interest is given by

$$\chi_e(\omega_2) = \rho \tilde{\chi}_1(r = a, \omega_2) F(\omega_2)^2 |F(\omega_1)|^2$$

(10)

where $F(\omega)$ denotes the local field enhancement factor in the linear system. By using the Maxwell–Garnett approach, it can be given by

$$F(\omega) = \frac{3\varepsilon_2}{\varepsilon_1 - \varepsilon_1 \rho\alpha + (2 + \rho\alpha)\varepsilon_2}$$

(11)

In eq 10, the equivalent third-order nonlinear susceptibility $\tilde{\chi}_1(r = a, \omega_2)$ can be obtained if the gradation profile $\chi_1(r, \omega_2)$ (which indicates the intrinsic NDFWM susceptibility) is given through solving the nonlinear differential effective dipole approximation\(^33\)

$$\frac{d\tilde{\chi}_1(r, \omega_2)}{dr} = \tilde{\chi}_1(r, \omega_2)[3d\tilde{\varepsilon}_1(r, \omega_2)/dr]/[2\varepsilon_2 + \tilde{\varepsilon}_1(r, \omega_2)] + \tilde{\chi}_1(r, \omega_2)[(d\tilde{\varepsilon}_1(r, \omega_2)/dr)/[2\varepsilon_2 + \tilde{\varepsilon}_1(r, \omega_2)]^* + \tilde{\chi}_1(r, \omega_2)(6Y + 2Y^* - 3)/r + 3\chi_1(r, \omega_2)/(5r) \times [\tilde{\varepsilon}_1(r, \omega_2) + 2\varepsilon_1(r, \omega_2)]/[3\varepsilon_1(r, \omega_2)]^2 \times \left\{ \tilde{\varepsilon}_1(r, \omega_2) + 2\varepsilon_1(r, \omega_2) \right\}/[3\varepsilon_1(r, \omega_2)]^2 \times (5 + 18X^2 + 18|X|^2 + 4X^3 + 12|X|^2 + 24X^2|X|^2)$$

(12)

with

$$X = \frac{\tilde{\varepsilon}_1(r, \omega_2) - \varepsilon_1(r, \omega_2)}{\varepsilon_1(r, \omega_2) + 2\varepsilon_1(r, \omega_2)}$$

(13)

Figure 5. Same as Figure 4 but for various $C_\omega$. Parameters: $t = 2.0$, $\gamma = 0.02\omega_p(0)$, and $\varepsilon_2 = 2.25$. 

as the imaginary part of the THG susceptibility Im(\(\chi_{zzzz}\)) that only the intrinsic SHG (or THG) susceptibility, namely, the \(z\) component of the effective THG susceptibility. We assume that only the intrinsic SHG (or THG) susceptibility, namely, \(d_\omega(r)\) or \(\chi_{zzzz}(r)\) of the graded particles are nonzero. That is to say, only the diagonal components in the graded particles are considered. So far, the equivalent susceptibility \(\tilde{d}_{ij}(2\omega, r)\), of the graded particle can be written as

\[
Y = \frac{\varepsilon_1(r, \omega_x) - \varepsilon_2(r, \omega_x)}{\varepsilon_1(r, \omega_x) + \varepsilon_2(r, \omega_x)}\]

In the following, without loss of generality, we focus on the \(z\) component of the effective THG susceptibility. We assume that only the intrinsic SHG (or THG) susceptibility, namely, \(d_\omega(r)\) or \(\chi_{zzzz}(r)\) of the graded particles are nonzero. That is to say, only the diagonal components in the graded particles are considered. So far, the equivalent susceptibility \(\tilde{d}_{ij}(2\omega, r)\), of the graded particle can be written as

\[
\frac{d\tilde{d}_{ik}(2\omega, r)}{dr} = \frac{2d\varepsilon_1(r, \omega)}{2\varepsilon_2 + \varepsilon_1(r, \omega)} + \frac{2y(\omega, r) + y(2\omega, r) - 3}{r} + \frac{3G_{ik}(2\omega, r)}{rf(2\omega, r)f^2(\omega, r)}
\]

Here, \(\tilde{d}_{ijk}(2\omega, r)\) represents \(\tilde{d}_{ijk}(\omega+\omega, r)\). When considering the \(z\) component, we obtain the form of \(G_{zz}\) as

\[
G_{zz}(2\omega, r) = d_{zz}(2\omega, r)\left[\frac{2\tilde{\varepsilon}(\omega, r) + \tilde{\varepsilon}(2\omega, r)}{35} + \frac{28}{35}\tilde{\varepsilon}(\omega, r)\tilde{\varepsilon}(2\omega, r) + \frac{8}{35}\tilde{\varepsilon}(\omega, r)\tilde{\varepsilon}(2\omega, r) - 3\varepsilon(\omega, r)\varepsilon(2\omega, r) - 3\varepsilon(\omega, r)\varepsilon(2\omega, r) + 2\varepsilon(\omega, r)\varepsilon(2\omega, r)\right]
\]

where \(\varepsilon(\omega, r) = (\varepsilon_1(\varepsilon_1(\omega, r) + 2\varepsilon_1(\omega, r)))/(\varepsilon_1(\varepsilon_1(\omega, r) + 2\varepsilon_1(\omega, r))), y(\omega, r) = 2(\varepsilon_1(\varepsilon_1(\omega, r) - \varepsilon_1(\varepsilon_1(\omega, r) - 2\varepsilon_1(\varepsilon_1(\omega, r)))/(\varepsilon_1(\varepsilon_1(\omega, r) - 2\varepsilon_1(\varepsilon_1(\omega, r)) + 2\varepsilon_1)), z(\omega, r) = (\varepsilon_1(\varepsilon_1(\omega, r) - \varepsilon_1(\varepsilon_1(\omega, r)))/(\varepsilon_1(\varepsilon_1(\omega, r) + 2\varepsilon_1)), and \(f(\omega, r) = (3\varepsilon_2)/(\varepsilon_1(\varepsilon_1(\omega, r) + 2\varepsilon_1)). Here, the indice \(2\omega\) corresponds to the second harmonic for the nonlinear susceptibility.

Note that \(d_{ij}(2\omega, r)\) denotes the equivalent SHG susceptibility of the whole graded metallic spherical particle with radius \(r\), \(r \leq a\). For convenience, we shall denote \(d_{ij}(2\omega, r = a)\) as \(d_{ij}(2\omega)\) in the following. The equivalent THG susceptibility, \(\tilde{G}_{ijk}(3\omega, r)\), of the graded metallic spherical particle can be written as
Figure 7. Same as Figure 6 but for various $C_{\infty}$. Parameters: $t = 2.0, \gamma = 0.02\omega_0(0), \epsilon_2 = 2.25$.

\[
\frac{d\tilde{G}_c(2\omega, r)}{dr} = \frac{2}{\epsilon_1(r, 2\omega) + 2\epsilon_2} \frac{d[\tilde{d}_c(2\omega, r)\tilde{d}_c(\omega, r)]}{dr} - \frac{2\tilde{d}_c(2\omega, r)\tilde{d}_c(\omega, r)\tilde{d}_c(r, 2\omega)}{\epsilon_1(r, 2\omega) + 2\epsilon_2} \frac{d\tilde{d}_c(r, 2\omega)}{dr} + \frac{3\tilde{d}_c(3\omega, r)}{\epsilon_1(r, 2\omega) + 2\epsilon_2} + \frac{2\tilde{d}_c(2\omega, r)\tilde{d}_c(\omega, r)\tilde{d}_c(3\omega, r)}{\epsilon_1(r, 2\omega) + 2\epsilon_2} + \frac{3H_c}{r(3\omega, r)^2(\omega, r)}
\]  

(17)

where $H_c$ is given by

\[
H_c = \frac{34}{385} \frac{d\tilde{d}_c(2\omega, r)\tilde{d}_c(\omega, r) + d\tilde{d}_c(2\omega, r)d\tilde{d}_c(\omega, r)}{\epsilon_1(r, 2\omega) + 2\epsilon_2} \times
\]

\[
\epsilon(\omega, r)[11x(2\omega, r) + 4z(2\omega, r)]z(3\omega, r) + 27 \left[ x_{\text{acc}}(\omega, r) + x_{\text{acc}}(\omega, r) - 2d_{\text{acc}}(2\omega, r) + d_{\text{acc}}(2\omega, r)\right] \epsilon(2\omega, r) - \epsilon_2
\]

\[
\frac{1}{35} \left[ x_{\text{acc}}(\omega, r) - 2d_{\text{acc}}(2\omega, r) + d_{\text{acc}}(2\omega, r)\right] \times [35x_{\text{acc}}(\omega, r)]z(3\omega, r) +
\]

\[
924x(\omega, r)x(2\omega, r)x(3\omega, r) + 176x(\omega, r)x(3\omega, r) + 158x(\omega, r)x(3\omega, r) + 16z(\omega, r)x(3\omega, r) + 48z(\omega, r)x(3\omega, r)
\]

Until now, the effective THG susceptibility of the system of our interest could be determined by
response, we take the intrinsic susceptibility will remain unchanged.

As a model system. Incidently, if we consider the lattice being real and positive frequency-independent constant $R$ take $\chi$ as a medium concept, and it is valid in the quasi-static approximation. The present method is based on the effective nonlinear optical properties of the system have been formulated dipole field of a tetragonal unit cell by taking into account the Ewald Korneld technique (eq 5) to compute the local electric field.

So far, for the periodic lattice structure, we have adopted the Ewald—Korneld technique (eq 5) to compute the local electric field of a tetragonal unit cell by taking into account the dipole—dipole interaction in the periodic lattice, and the effective nonlinear optical properties of the system have been formulated in the above. The present method is based on the effective medium concept, and it is valid in the quasi-static approximation.

### III. Numerical Results

For all of our numerical calculations (Figures 2–11), we shall take $\alpha_L = 0.95351$ or $q = 0.87358$ (namely, the bct structure) as a model system. Incidently, if we consider the lattice being beyond the BCT, the qualitative results obtained in this work will remain unchanged.

In order to focus on the enhancement of the NDFWM response, we take the intrinsic susceptibility $\chi(r, \omega_1)$ to be a real and positive frequency-independent constant $\chi_1$. Figure 2 displays the linear and nonlinear optical responses. These curves are obtained by tuning the gradation profile parameter $C_0$ from 0.0 to 0.8. In detail, as $C_0 \to 0$, the gradation profile is not considered, and the optical absorption peak is very sharp in the high frequency region (Figure 2a). As $C_0$ increases, the absorption peak is red-shifted (namely, shifted to the lower frequency region), and its magnitude is reduced at the same time. The nonlinearity enhancement is investigated in Figure 2b–d, which clearly shows that the nonzero $C_0$ could lead to the enhanced nonlinear responses, and the frequency at which the enhancement peak appears could be red-shifted accordingly. All of these results indicate that nonlinearity enhancement can be achieved by choosing an appropriate gradation profile parameter $C_0$. Although the enhancement of optical nonlinearity is always accompanied by the optical absorption, the figure of merit (FOM), as shown in Figure 2e, is more attractive at some frequencies for $C_0 \neq 0$ than that for $C_0 = 0$. Especially, as $C_0$ is large enough, that is, $C_0 = 0.8$, most of the frequency region owns an attractive FOM, in comparison with the case of $C_0 = 0$ (namely, under the condition of homogeneity).

Figure 3 is the same as Figure 2 but for various $\omega_1$ (frequency of pump fields). This figure shows that there exist suitable frequencies $\omega_1$ of pump fields which may cause the enhancement of nonlinearity as well as an attractive FOM. Figure 3a also indicates that $\omega_1$ has almost no effect on the absorption spectrum. In the meantime, $\omega_1$ cannot apparently change the

**Figure 8.** The enhancement of an effective THG susceptibility $\chi_{\text{eff}}$ due to the intrinsic THG, for which the only nonzero component $\chi_{\text{eff}}(3\omega, r)$ is a real and positive frequency-independent constant, $\chi_0$. (a) The linear optical absorption $\text{Im}(\chi)$, (b) the real part of the THG susceptibility $\text{Re}(\chi_{\text{eff}}/\chi_0)$, (c) the imaginary part of the THG susceptibility $\text{Im}(\chi_{\text{eff}}/\chi_0)$, (d) the modulus of the THG susceptibility $|\chi_{\text{eff}}/\chi_0|$, and (e) FOM $\equiv |\chi_{\text{eff}}|/|\chi_0\text{Im}(\epsilon_3)|$ versus the normalized angular frequency $\omega/\omega_0$ for various $t$. Parameters: $\gamma = 0.02\omega_0(0), C_0 = 0.2$, and $\epsilon_2 = 2.25$.

\[
\chi_{\text{eff}} = \rho \left\{ \frac{3\epsilon_2}{\epsilon_1(r = a, 3\omega) + 2\epsilon_2} \left[ \frac{3\epsilon_2}{\epsilon_1(r = a, \omega) + 2\epsilon_2} \right] \right\} \times
\left\{ \frac{2d_{zzzz}(2\omega, r = a)d_{zzzz}(\omega, r = a)}{\epsilon_1(r = a, 2\omega) + 2\epsilon_2} \right\}
\]

(19)
peak for the nonlinearity enhancement as well as the FOM, as shown in Figure 3b–e.

Figure 4 shows the enhancement of an effective THG susceptibility \( \chi_{xxx} \) due to the SHG susceptibility, for which the only nonzero component \( d_{xxx}(2\omega,r) \) is a real and positive frequency-independent constant, \( d_{x} \). From this figure, we find that the linear optical absorption \( \text{Im}(\epsilon_{e}) \) can be tuned by the thickness parameter \( t \) (Figure 4a) and that the decrease of \( t \) could enhance the effective THG susceptibility in certain frequency ranges (Figure 4b–d). Meanwhile, the FOM can become more attractive.

Figure 5 is the same as Figure 4 but for various \( C_{\omega} \). Here, larger \( C_{\omega} \) denotes stronger inhomogeneity in metallic cores. According to this figure, it is apparent to observe that stronger inhomogeneity can lead to enhanced nonlinearity in certain frequency ranges (Figure 5b–d), and the peak of nonlinearity enhancement can be red-shifted (Figure 5b–d). In the meantime, the peak of FOM (Figure 5e) or absorption (Figure 5a) is also red-shifted accordingly.

Figure 6 displays an effective THG susceptibility \( \chi_{xxx} \) due to the SHG susceptibility, for which the only nonzero component \( d_{xxx}(2\omega,r) \) is a real and positive frequency-independent constant, \( d_{x} \). This figure shows no enhancement of nonlinearity (Figure 6b–d). It means that the nonzero \( x \) component of SHG susceptibilities cannot enhance the effective THG susceptibility, even though the thickness parameter \( t \) is adjustable. Also, the FOM is not attractive. Similar behavior appears in Figure 7, which is plotted for various \( C_{\omega} \).

Figure 8 shows the enhancement of an effective THG susceptibility \( \chi_{zzzz} \) due to the intrinsic THG, for which the only nonzero component \( \chi_{zzzz}(3\omega,r) \) is a real and positive frequency-independent constant, \( \chi_{z} \). We find that the linear optical absorption can also be changed by tuning the thickness parameter \( t \). Moreover, decreasing \( t \) leads to increasing nonlinearity enhancement. In the meantime, the FOM becomes more attractive.

Figure 9 is the same as Figure 8 but for various \( C_{\omega} \). From this figure, it is evident that stronger inhomogeneity can cause the peak of nonlinearity enhancement or the FOM to be red-shifted.

Figure 10 displays an effective THG susceptibility \( \chi_{zzzz} \) due to the intrinsic THG, for which the only nonzero component \( \chi_{zzzz}(3\omega,r) \) is a real and positive frequency-independent constant, \( \chi_{z} \). This figure shows no enhancement of nonlinearity. A similar conclusion can be found for Figure 11, which is plotted for various \( C_{\omega} \). Both Figures 10 and 11 show that the only nonzero \( x \) component of the intrinsic THG susceptibility may not be used to enhance the effective THG susceptibility, even by changing \( t \) or \( C_{\omega} \).

IV. Discussion and Conclusion

Here, we would like to mention that some experimental results have been reported, which qualitatively agree with our theoretical prediction related to the gradation (inhomogeneity) effect.35 They35 have reported that for Ag/BaTiO3 composite films...
fabricated using pulsed laser deposition, if the prolate-spheroidal metallic particles in the film are distributed with some gradation profile, the optical nonlinear susceptibility can be enhanced at certain frequencies of incident light.

For the periodic lattice structure, we have used the Ewald-Kornfeld technique (eq 5) to compute the local electric field of a tetragonal unit cell by taking into account the dipole-dipole interaction in the periodic lattice, and the nonlinear optical properties of the system have been investigated. Our method is based on the effective medium concept, and it is valid in the quasi-static approximation. In the case of weak nonlinearity discussed in this work, the validity of our calculation for the effective nonlinear optical responses (eqs 10 and 19) was confirmed by the perturbation expansion method.36 The derivation of the equivalent nonlinear susceptibility for graded particles (eqs 12, 15, and 17) was originally confirmed by a first-principles approach based on solving the Maxwell equations,33,37 and then, it was extended to the cases of SHG and THG on the same footing.34

In this work, we have set the dielectric shell of the coated nanoparticles to have the same dielectric constant as the host fluid, which enables us to focus on the lattice (local field) effect in the presence of gradation by neglecting the multipolar interaction between the suspended nanoparticles. In fact, we might indeed set the dielectric constant of the shells to differ from that of the host. In this case, a method of multiple images of dipoles38 might be developed, for example, on the same footing as the generally used coupled point dipole model. Nevertheless, the results, which have been achieved for the lattice (local field) effect of our interest, should remain unchanged. This can be concluded from the validity of the Ewald-Kornfeld formula (eq 5).

It is useful to have inhomogeneous metallic particles in order to achieve desired linear or nonlinear optical responses by tuning the degree of gradation (inhomogeneity). However, it is not expected to increase the enhancement of any nonlinear coefficients. An increase of the enhancement can appear when appropriate enhancement of local fields is caused by gradation (inhomogeneity). In other words, if the enhancement of local fields is limited (or even caused to reduce) in specific structures, it will be impossible to increase the enhancement of nonlinear coefficients, even for inhomogeneous metallic particle.

In summary, we have theoretically investigated the third-order nonlinear optical susceptibilities for NDFWM and THG in colloidal crystals which are made of graded metalloidielectric nanoparticles. On the basis of the Ewald-Kornfeld formulation (eq 5), numerical results show that such materials can have both an enhancement and a red shift of optical nonlinearity due to the gradation in the metallic core and the lattice effect arising from period structures.

Figure 10. An effective THG susceptibility $\chi_{zzzz}$ due to the intrinsic THG, for which the only nonzero component $\chi_{zzzz}$ is a real and positive frequency-independent constant, $\chi_z$. (a) The linear optical absorption $\text{Im}(\epsilon_{zzzz})$, (b) the real part of the THG susceptibility $\text{Re}(\chi_{zzzz}/\chi_z)$, (c) the imaginary part of the THG susceptibility $\text{Im}(\chi_{zzzz}/\chi_z)$, (d) the modulus of the THG susceptibility $|\chi_{zzzz}/\chi_z|$, and (e) FOM $\equiv |\chi_{zzzz}/[\chi_z \text{Im}(\epsilon_z)]$ versus the normalized angular frequency $\omega/\omega_p(0)$ for various $t$. Parameters: $\gamma = 0.02\omega_p(0)$, $C_{\omega_p} = 0.2$, and $\epsilon_2 = 2.25$. 

Nonlinear Optical Susceptibilities of Colloidal Crystals

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References and Notes


Figure 11. Same as Figure 10 but for various $C_\nu$. Parameters: $t = 2.0$, $\gamma = 0.02\omega_0(0)$, and $\varepsilon = 2.25$.

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