Abstract

We have developed a nonlinear differential effective dipole approximation (NDEDA), in an attempt to investigate the effective linear and third-order nonlinear susceptibility of composite media in which graded spherical inclusions with weak nonlinearity are randomly embedded in a linear host medium. Alternatively, based on a first-principles approach, we derived exactly the linear local field inside the graded particles having power-law dielectric gradation profiles. As a result, we obtain also the effective linear dielectric constant and third-order nonlinear susceptibility. Excellent agreement between the two methods is numerically demonstrated. As an application, we apply the NDEDA to investigate the surface plasma resonant effect on the optical absorption, optical nonlinearity enhancement, and figure of merit of metal-dielectric composites. It is found that the presence of gradation in metal particles yields a broad resonant band in the optical region, and further enhances the figure of merit.

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I. INTRODUCTION

Graded materials, whose material properties can vary continuously in space, are abundant in nature. These materials have attracted much interest as one of the advanced inhomogeneous composite materials in various engineering applications [1]. With the advent of fabrication techniques, these materials can be well produced to tailor their properties for specific needs via the design of the material and microstructure gradients. Such a design makes graded materials quite different in physical properties from the homogeneous materials and other conventional composite materials. Moreover, the composite media consisting of graded inclusions can be more useful and interesting than those of homogeneous inclusions. Although various theories have been established to investigate the optical and dielectric properties of the composite media of homogeneous inclusions [2,3], they fail to deal with the inhomogeneous composites of graded inclusions. Recently, a first-principles approach [4,5] and a differential effective dipole approximation [6,7] have been presented in order to investigate the dielectric response of graded materials.

The problem becomes more complicated by the presence of nonlinearity in realistic composites. Besides inhomogeneity, such nonlinearity plays also an important role in the effective material properties of composite media [8–11]. It is thus necessary to establish a new theory to study the effective nonlinear properties of graded composite media. In fact, the introduction of dielectric gradation profiles in nonlinear composites is able to provide an alternative way to control the local field fluctuation, and hence let us obtain the desired effective nonlinear response.

In fact, the previous one-shell model [12] and multi-shell model [13], which were used to study the effective nonlinear optical property, can be seen as an initial model of graded inclusions. In this paper, we will put forth a nonlinear differential effective dipole approximation (NDEDA) to investigate the effective linear and nonlinear dielectric properties of composite media containing nonlinear graded spherical particles (inclusions). For such particles, the linear and nonlinear physical properties will continuously vary along their radius.
The paper is organized as follows. In section II, we describe the model and define briefly
the effective linear dielectric constant and third-order nonlinear susceptibility. In section III,
the NDEDA is presented to investigate the effective linear dielectric constant and third-order
nonlinear susceptibility of nonlinear graded composite media in the dilute limit. In section
IV, based on a first-principles approach, we derive the exact solutions for composite media
having power-law gradation profiles inside the inclusions, which is followed by the numerical
results in section V. Finally, some conclusion and discussion is shown in Section VI.

II. MODEL AND DEFINITION OF EFFECTIVE LINEAR AND NONLINEAR
RESPONSES

Let us consider a nonlinear composite system, in which identical graded spherical inclu-
sions with radius $a$, are randomly embedded in a linear host medium of dielectric constant
$\varepsilon_2$. The local constitutive relation between the displacement ($D$) and the electric field ($E$)
inside the graded particle is given by

$$D = \epsilon(r)E + \chi(r)|E|^2E,$$  (1)

where $\epsilon(r)$ and $\chi(r)$ are, respectively, the linear dielectric constant and third-order nonlinear
susceptibility. Note both $\epsilon(r)$ and $\chi(r)$ are radial functions. Here we assume that the
weak nonlinearity condition is satisfied [14]. In other words, the contribution of the second
(nonlinear) part $[\chi_s(r)|E|^2]$ in the right-hand side of Eq. (1) is much less than that of the
first (linear) part $\epsilon(r)$. We restrict further our discussion to the quasi-static approximation,
under which the whole composite medium can be regarded as an effective homogeneous one
with effective linear dielectric constant $\epsilon_e$ and effective third-order nonlinear susceptibility
$\chi_e$. To show the definitions of $\epsilon_e$ and $\chi_e$, we have [14]

$$\langle D \rangle = \epsilon_eE_0 + \chi_e|E_0|^2E_0,$$  (2)

where $\langle \cdots \rangle$ represents the spatial average, and $E_0 = E_0e_z$ is the external applied field along
$z$ axis.
The effective linear dielectric constant $\epsilon_e$ is given by

$$\epsilon_e E_0 = \frac{1}{V} \int_V \epsilon_i \mathbf{E}_{\text{lin},i} dV = f \langle \epsilon(r) \mathbf{E}_{\text{lin}1} \rangle + (1 - f) \epsilon_2 \langle \mathbf{E}_{\text{lin}2} \rangle,$$

where $f$ is the volume fraction of the graded particles and the subscript stands for the linear local field [i.e., obtained for the same system but with $\chi(r) = 0$].

In view of the existence of nonlinearity inside the graded particles, $\chi_e$ can then be written as [14,15]

$$\chi_e E_0^4 = \frac{1}{V} \int_V \chi_i |\mathbf{E}_{\text{lin},i}|^2 \mathbf{E}_{\text{lin},i}^2 dV = \frac{1}{V} \int_{\Omega} \chi(r) |\mathbf{E}|^2 \mathbf{E}_{\text{lin}1}^2 dV = f \langle \chi(r) |\mathbf{E}|^2 \mathbf{E}_{\text{lin}1}^2 \rangle.$$

In the next section, we will develop a NDEDA (nonlinear differential effective dipole approximation), in an attempt to derive the equivalent linear dielectric constant $\bar{\epsilon}(a)$ and third-order nonlinear susceptibility $\bar{\chi}(a)$ of the nonlinear graded inclusions. Then, the effective linear dielectric constant and third-order nonlinear susceptibility of the composite media of nonlinear graded inclusions will be derived accordingly in the dilute limit.

III. NONLINEAR DIFFERENTIAL EFFECTIVE DIPOLE APPROXIMATION

To establish the NDEDA, we first mimic the gradation profile by a multi-shell constriction. That is, we build up the dielectric profile by adding shells gradually [6]. We start with an infinitesimal spherical core with linear dielectric constant $\epsilon(0)$ and third-order nonlinear susceptibility $\chi(0)$, and keep on adding spherical shells with linear dielectric constant $\epsilon(r)$ and third-order nonlinear susceptibility $\chi(r)$ at radius $r$, until $r = a$ is reached. At radius $r$, the inhomogeneous spherical particle with space-dependent dielectric gradation profiles $\epsilon(r)$ and $\chi(r)$ can be replaced by a homogenous sphere with the equivalent dielectric properties $\bar{\epsilon}(r)$ and $\bar{\chi}(r)$. Here the homogenous sphere should induce the same dipole moment as the original inhomogeneous sphere.

Next, we add to the sphere a spherical shell of infinitesimal thickness $dr$, with dielectric constant $\epsilon(r)$ and nonlinear susceptibility $\chi(r)$. In this sense, the coated inclusions is
composed of a spherical core with radius $r$, linear dielectric constant $\epsilon(r)$ and nonlinear susceptibility $\chi(r)$, and a shell with outermost radius $r + dr$, linear dielectric constant $\epsilon(r)$ and nonlinear susceptibility $\chi(r)$. Since these coated inclusions are randomly embedded in a linear host medium, under the quasi-static approximation, we can readily obtain the linear electric potentials in the core, shell and host medium by solving the Laplace equation [16]

\[
\phi_c = -E_0 A R \cos \theta, \quad R < r, \\
\phi_s = -E_0 \left( BR - \frac{C r^3}{R^2} \right) \cos \theta, \quad r < R < r + dr, \\
\phi_h = -E_0 \left( R - \frac{D (r + dr)^3}{R^2} \right) \cos \theta, \quad R > r + dr,
\]

where

\[
A = \frac{9 \epsilon_2 \epsilon(r)}{Q}, \quad B = \frac{3 \epsilon_2 [\tilde{\epsilon}(r) + 2 \epsilon(r)]}{Q}, \quad C = \frac{3 \epsilon_2 [\tilde{\epsilon}(r) - \epsilon(r)]}{Q}, \\
D = \frac{[\epsilon(r) - \epsilon_2] [\tilde{\epsilon}(r) + 2 \epsilon(r)] + \lambda [\epsilon_2 + 2 \epsilon(r)] [\tilde{\epsilon}(r) - \epsilon(r)]}{Q},
\]

with interfacial parameter $\lambda \equiv [r/(r + dr)]^3$, and

\[
Q = [\epsilon(r) + 2 \epsilon_2 [\tilde{\epsilon}(r) + 2 \epsilon(r)] + 2 \lambda [\epsilon(r) - \epsilon_2] [\tilde{\epsilon}(r) - \epsilon(r)].
\]

The effective (overall) linear dielectric constant of the system is determined by the dilute-limit expression [17]

\[
\epsilon_e = \epsilon_2 + 3 p \epsilon_2 D, \quad (6)
\]

where $p$ is the volume fraction of graded particles with radius $r$. The equivalent dielectric constant $\tilde{\epsilon}(r + dr)$ for the graded particles with radius $r + dr$ can be obtained self-consistently by the vanishing of the dipole factor $D$ by replacing $\epsilon_2$ with $\tilde{\epsilon}(r + dr)$. Taking the limit $dr \to 0$ and keeping to the first order in $dr$, we obtain

\[
\tilde{\epsilon}(r + dr) = \epsilon(r) + 3 \epsilon(r) \lambda \cdot \frac{\tilde{\epsilon}(r) - \epsilon(r)}{\tilde{\epsilon}(r)(1 - \lambda) + \epsilon(r)(2 + \lambda)} \\
= \epsilon(r) - \frac{\tilde{\epsilon}(r) - \epsilon(r)}{r} \cdot \left[ 3 + \frac{\tilde{\epsilon}(r) - \epsilon(r)}{\epsilon(r)} \right] dr. \quad (7)
\]
Thus, we have the differential equation for the equivalent dielectric constant $\bar{\varepsilon}(r)$ as [6]

$$
\frac{d\bar{\varepsilon}(r)}{dr} = \frac{[\varepsilon(r) - \bar{\varepsilon}(r)] \cdot [\bar{\varepsilon}(r) + 2\varepsilon(r)]}{r\bar{\varepsilon}(r)}.
$$

(8)

Note that Eq. (8) is just the Tartar formula, derived for assemblages of spheres with varying radial and tangential conductivity [18].

Next, we speculate on how to derive the equivalent nonlinear susceptibility $\bar{\chi}(r)$. After applying Eq. (4) to the coated particles with radius $r + dr$, we have

$$
\bar{\chi}(r + dr) \frac{\langle |E|^2 |E|^2 \rangle_{R \leq r + dr}}{|E_0|^2 |E_0|^2} = \bar{\chi}(r) \frac{3\varepsilon_2}{|\bar{\varepsilon}(r + dr) + 2\varepsilon_2|^2} \left( \frac{3\varepsilon_2}{|\bar{\varepsilon}(r + dr) + 2\varepsilon_2|^2} \right)^2
+ \bar{\chi}(r) |K|^2 K^2 \frac{3d\bar{\varepsilon}(r)/dr}{2\varepsilon_2 + \bar{\varepsilon}(r)} + \left( \frac{d\bar{\varepsilon}(r)/dr}{2\varepsilon_2 + \bar{\varepsilon}(r)} \right)^*.
$$

(9)

As $dr \to 0$, the left-hand side of the above equation admits

$$
\bar{\chi}(r + dr) \frac{\langle |E|^2 |E|^2 \rangle_{R \leq r + dr}}{|E_0|^2 |E_0|^2} = \bar{\chi}(r + dr) \left( \frac{3\varepsilon_2}{|\bar{\varepsilon}(r + dr) + 2\varepsilon_2|} \right)^2
+ |K|^2 K^2 \frac{d\bar{\chi}(r)}{dr} \cdot dr,
$$

(10)

with $K = (3\varepsilon_2)/[\varepsilon(r) + 2\varepsilon_2]$. The first part of the right-hand side of Eq. (9) is written as

$$
\lambda \frac{\langle |E|^2 |E|^2 \rangle_{R \leq r}}{|E_0|^2 |E_0|^2} = \bar{\chi}(r) |K|^2 K^2 \left[ 1 + (6y + 2y^* - 3) \frac{dr}{r} \right],
$$

(11)

where

$$
y = \frac{[\varepsilon(r) - \varepsilon_2][\bar{\varepsilon}(r) - \varepsilon_2]}{\varepsilon(r)\bar{\varepsilon}(r) + 2\varepsilon_2}.
$$

The second part of the right-hand side of Eq. (9) has the form [17]

$$
(1 - \lambda) \frac{\langle \chi(r) |E|^2 |E|^2 \rangle_{R < R \leq r + dr}}{|E_0|^2 |E_0|^2} = \frac{3\chi(r)}{5r} \int dz |z|^2 z^2 \times (5 + 18x^2 + 18|x|^2 + 4x^3 + 12|x|^2 + 24|x|^2 x^2),
$$

(12)

where

$$
x = \frac{\bar{\varepsilon}(r) - \varepsilon(r)}{\bar{\varepsilon}(r) + 2\varepsilon(r)} \quad \text{and} \quad z = \frac{\varepsilon_2[\bar{\varepsilon}(r) + 2\varepsilon(r)]}{\varepsilon(r)\bar{\varepsilon}(r) + 2\varepsilon_2}.
$$

Substituting Eqs. (10), (11) and (12) into Eq. (9), we have a differential equation for the equivalent nonlinear susceptibility $\bar{\chi}(r)$, namely,
\[
\frac{d\bar{\chi}(r)}{dr} = \bar{\chi}(r) \left[ \frac{3d\bar{\epsilon}(r)/dr}{2\epsilon_2 + \bar{\epsilon}(r)} + \left( \frac{d\bar{\epsilon}(r)/dr}{2\epsilon_2 + \bar{\epsilon}(r)} \right)^* \right] + \bar{\chi}(r) \cdot \frac{6y + 2y^* - 3}{r} + \frac{3\chi(r)}{5r} \cdot \left| \frac{\bar{\epsilon}(r) + 2\epsilon(r)}{3\epsilon(r)} \right|^2 \\
\cdot \left( \frac{\bar{\epsilon}(r) + 2\epsilon(r)}{3\epsilon(r)} \right)^2 \left( 5 + 18x^2 + 18|x|^2 + 4x^3 + 12x|x|^2 + 24|x|^2x^2 \right). \tag{13}
\]

So far, the equivalent \( \bar{\epsilon}(r) \) and \( \bar{\chi}(r) \) of graded spherical particles of radius \( r \) can be calculated, at least numerically, by solving the differential equations Eqs. (8) and (13), as long as \( \epsilon(r) \) (dielectric-constant gradation profile) and \( \chi(r) \) (nonlinear-susceptibility gradation profile) are given. Here we would like to mention that, even though \( \chi(r) \) is independent of \( r \), the equivalent \( \bar{\chi}(r) \) should still be dependent on \( r \) because of \( \epsilon(r) \) as a function of \( r \). Moreover, for both \( \epsilon(r) = \epsilon_1 \) and \( \chi(r) = \chi_1 \) (i.e., they are both constant and independent of \( r \)), Eqs. (8) and (13) will naturally reduce to the solutions \( \bar{\epsilon}(r) = \epsilon_1 \) and \( \bar{\chi}(r) = \chi_1 \).

To obtain \( \bar{\epsilon}(r = a) \) and \( \bar{\chi}(r = a) \), we integrate Eqs. (8) and (13) numerically at given initial conditions \( \bar{\epsilon}(r \to 0) \) and \( \bar{\chi}(r \to 0) \). Once \( \bar{\epsilon}(r = a) \) and \( \bar{\chi}(r = a) \) are calculated, we can take one step forward to work out the effective linear and nonlinear responses \( \epsilon_e \) and \( \chi_e \) of the whole composite in the dilute limit, i.e. [14],

\[
\epsilon_e = \epsilon_2 + 3\epsilon_2 f \frac{\bar{\epsilon}(r = a) - \epsilon_2}{\bar{\epsilon}(r = a) + 2\epsilon_2}, \tag{14}
\]

and

\[
\chi_e = f \bar{\chi}(r = a) \left| \frac{3\epsilon_2}{\bar{\epsilon}(r = a) + 2\epsilon_2} \right|^2 \left( \frac{3\epsilon_2}{\bar{\epsilon}(r = a) + 2\epsilon_2} \right)^2. \tag{15}
\]

**IV. EXACT SOLUTION FOR POWER-LAW GRADATION PROFILES**

Based on the first-principles approach, we have found that, for a power-law dielectric gradation profile, i.e., \( \epsilon(r) = A(r/a)^n \), the potential in the graded inclusions and the host medium can be exactly given by [4]

\[
\phi_i(r) = -\xi_1 E_0 r^s \cos \theta, \quad r < a,
\]

\[
\phi_h(r) = -E_0 r \cos \theta + \frac{\xi_2}{r^2} E_0 \cos \theta, \quad r > a, \tag{16}
\]
where the coefficients $\xi_1$ and $\xi_2$ have the form

$$\xi_1 = \frac{3a^1 - \varepsilon_2}{sA - 2\varepsilon_2}$$

and

$$\xi_2 = \frac{sA - \varepsilon_2}{sA - 2\varepsilon_2} a^3,$$

and $s$ is given by

$$s = \frac{1}{2} \left[ \sqrt{9 + 2n + n^2} - (1 + n) \right].$$

The local electric field inside the graded inclusions can be derived from the potential $E = -\nabla \phi$,

$$E_i = \xi_1 E_0 r^{s-1}(s \cos \theta e_r - \sin \theta e_\theta) = \xi_1 E_0 r^{s-1} \{(s - 1) \cos \theta \sin \theta \cos \phi e_x$$

$$+ (s - 1) \cos \theta \sin \theta \sin \phi e_y + [(s - 1) \cos^2 \theta + 1] e_z \},$$

(17)

where $e_r$, $e_\theta$, $e_x$, $e_y$ and $e_z$ are unix vectors. In the dilute limit, from Eq. (3), we can obtain the effective linear dielectric constant as follows

$$\epsilon_e = \epsilon_2 + \frac{1}{V E_0} \int_{\Omega_i} \left[ A(r/a)^n - \varepsilon_2 \right] e_z \cdot E_i dV$$

$$= \epsilon_2 + 3\epsilon_2 f \frac{2 + s}{sA + 2\varepsilon_2} \left( \frac{A}{2 + n + s} - \frac{\varepsilon_2}{2 + s} \right).$$

(18)

On the other hand, the substitution of Eq. (17) into Eq. (4) yields

$$\chi_e = \frac{1}{V} \int_{\Omega_i} \chi(r) |\xi_1|^2 \xi_1^2 (s^2 \cos^2 \theta + \sin^2 \theta)^2 r^{4s - 2} \sin \theta dr d\theta d\phi$$

$$= \frac{f}{5a^3} |\xi_1|^2 \xi_1^2 (8 + 4s + 3s^4) \cdot \int_0^a \chi(r)r^{4s - 2} dr.$$

(19)

For example, for a linear profile of $\chi(r)$, i.e., $\chi(r) = k_1 + k_2 \cdot r/a$, Eq. (19) leads to

$$\chi_e = \frac{f}{20} \left( \frac{3\epsilon_2}{sA + 2\varepsilon_2} \right)^2 \left( \frac{3\epsilon_2}{sA + 2\varepsilon_2} \right)^2 (8 + 4s^2 + 3s^4) \left( \frac{k_2}{s} + \frac{4k_1}{4s - 1} \right).$$

(20)

In addition, for a power-law profile of $\chi(r)$, namely, $\chi(r) = k_1 (r/a)^{k_2}$, Eq. (19) produces

$$\chi_e = \frac{f}{5} \left( \frac{3\epsilon_2}{sA + 2\varepsilon_2} \right)^2 \left( \frac{3\epsilon_2}{sA + 2\varepsilon_2} \right)^2 k_1 \left( \frac{8 + 4s^2 + 3s^4}{k_2 - 1 + 4s} \right).$$

(21)
V. NUMERICAL RESULTS

We are now in a position to evaluate the NDEDA. For the comparison between the first-principles approach and the NDEDA, we first perform numerical calculations for the case where the dielectric constant exhibits power-law gradation profiles $\epsilon(r) = A(r/a)^n$, while the third-order nonlinear susceptibility shows two model gradation profiles: (a) linear profile $\chi(r) = k_1 + k_2 \cdot r/a$, and (b) power-law profile $\chi(r) = k_1(r/a)^{k_2}$. Without loss of generality, we take $\epsilon_2 = 1$ and $a = 1$ for numerical calculations. The fourth-order Runge-Kutta algorithm is adopted to integrate the differential equations [Eqs. (8) and (13)] with step size 0.01. Meanwhile, the initial core radius is set to be 0.001. It was verified that this step size guarantees accurate numerics.

In Fig. 1, the effective linear dielectric constant ($\epsilon_e$) is plotted as a function of $A$ for various indices $n$. It is shown that $\epsilon_e$ exhibits a monotonic increase for increasing $A$ (and decreasing $n$). This can be understood by using the equivalent dielectric constant $\bar{\epsilon}(r = a)$ which increases as $A$ increases ($n$ decreases). Moreover, the excellent agreement between the NDEDA [Eq. (8)] and the first-principles approach [Eq. (18)] is shown as well.

Next, the effective third-order nonlinear susceptibility ($\chi_e$) is plotted as a function of $A$ for the linear gradation profile $\chi(r) = k_1 + k_2 \cdot r/a$ (Fig. 2), and for the power-law profile $\chi(r) = k_1(r/a)^{k_2}$ (Fig. 3). We find that the effective nonlinear susceptibility decreases for increasing $A$. The reason is that, as mentioned above, for larger $A$, the graded inclusions possess larger equivalent dielectric constant, and the local field inside the nonlinear inclusions will become more weak, which results in a weaker effective nonlinear susceptibility ($\chi_e$). In addition, increasing $n$ leads generally to increasing $\chi_e$, and such a trend is clearly observed at large $A$. Again, we obtain the excellent agreement between the first-principles approach [Eqs. (20) and (21)] and the NDEDA [Eqs. (8) and (13)].

In what follows, we investigate the surface plasma resonance effect on the metal-dielectric composite. We adopt the Drude-like dielectric constant for graded metal particles, namely,
\[
\epsilon(r) = 1 - \frac{\omega_p^2(r)}{\omega[\omega + i\gamma(r)]},
\]

where \(\omega_p(r)\) and \(\gamma(r)\) are the radius-dependent plasma frequency and damping coefficient, respectively. For the sake of simplicity, set \(\chi(r) = \chi_1\) to be independent of \(r\), in an attempt to emphasize the enhancement of the effective optical nonlinearity, and \(\epsilon_2 = 1.77\) (the dielectric constant of water). We assume further \(\omega_p(r)\) to be

\[
\omega_p(r) = \omega_p(1 - k_\omega \cdot \frac{r}{a}), \quad r < a.
\]

This form is quite physical for \(k_\omega > 0\), since the center of grains can be better metallic so that \(\omega_p(r)\) is larger, while the boundary of the grain may be poorer metallic so that \(\omega_p(r)\) is much smaller. Such the variation can also appear because of the temperature effect [19]. For small particles, we have the radius-dependent \(\gamma(r)\) as [20]

\[
\gamma(r) = \gamma(\infty) + \frac{k_\gamma}{r/a}, \quad r < a,
\]

where \(\gamma(\infty)\) stands for the damping coefficient in the bulk material. Here \(k_\gamma\) is a constant which is related to the Fermi velocity \(v_F\). In this case, the exact solution being predicted by a first-principles approach is absent. Fortunately, we can resort to the NDEDA instead.

In Fig.3, we plot the optical absorption \([\sim \text{Im}(\epsilon_e)]\), the modulus of the effective third-order optical nonlinearity enhancement \(|\chi_e|/\chi_1\) and the figure of merit \(|\chi_e|/\text{Im}(\epsilon_e)\) versus the incident angular frequency \(\omega\). For various variance slopes \(k_\omega\), large surface plasma resonance peaks can appear around \(\omega \approx 0.4\omega_p\), as expected. However, when the radius dependence of \(\omega_p(r)\) is taken into account (i.e., \(k_\omega \neq 0\)), besides a sharp peak, a broad continuous resonant bands in the high frequency region is clearly observed. The broad spectra result from the effect of radius dependence of the plasma frequency. In Ref. [12], we found that, when the shell model is considered, there should be a broad continuous spectrum around the large pole in the spectral density function. In fact, the graded particles under consideration can be regarded as a certain limit of multi shells, which hence should lead to broader spectra in \(\text{Im}(\epsilon_e), |\chi_e|/\chi_1\) as well as \(|\chi_e|/\text{Im}(\epsilon_e)\). In addition, we note that, with increasing \(k_\omega\), both
the surface plasma frequency and the center of resonant bands are red-shifted. In particular, the resonant bands can become more broad due to strong inhomogeneity of the particles. From the figure, we conclude that, although the third-order optical nonlinearity is always accompanied with the optical absorption, the figure of merit in the high frequency region is still attractive due to the presence of \textit{weak} optical absorption. Thus, we believe that graded particles may have potential applications in obtaining the optimal figure of merit, and make the composite media more realistic for practical applications.

Finally, we focus on the effect of $\gamma(r)$ on the nonlinear optical property in Fig. 5. As evident from the results, the variation of $k_\gamma$ plays an important role in the magnitude of the effective optical properties, particularly at the surface plasma resonance frequency.

**VI. CONCLUSION AND DISCUSSION**

Here a few comments are in order. In this work, we have developed an NDEDA (nonlinear differential effective dipole approximation) to calculate the effective linear and nonlinear dielectric responses of composite media containing nonlinear graded inclusions. The results obtained from the NDEDA are compared with the exact solutions derived from a first-principles approach for the power-law dielectric gradation profiles, and the excellent agreement between them has been shown. We should remark that the exact solutions are also obtainable for the linear dielectric gradation profiles with small slopes (the derivation not shown here). In this case, the excellent agreement between the two methods can be shown as well since the NDEDA is valid indeed for arbitrary gradation profiles. In general, the exact solution is quite few in realistic composite research, and thus our NDEDA can be used as a benchmark.

It is instructive to develop the first-principles approach to nonlinear graded composites. The perturbation approach [21] in weakly nonlinear composites as well as the variational approach [22] in strongly nonlinear composites are just suitable for this problem.

The NDEDA is strictly valid in the dilute limit. To achieve the strong optical nonlinearity
enhancement, we need possibly nonlinear inclusions with high volume fractions. In this connection, the effect of the volume fraction is expected to cause a further broadening of the resonant peak, and possibly, a desired separation of the optical absorption peak from the nonlinearity enhancement due to mutual interactions [23]. Therefore, it is of particular interest to generalize the NDEDA for treating the case of high volume fractions.

To one’s interest, the NDEDA can be applied to biological cells. Since the interior of biological cells is often inhomogeneous and nonlinear in nature, they can be treated as particles having dielectric gradation profiles [7]. Moreover, in the case of cell membranes containing mobile charges introduced by the adsorbed hydrophobic ions, the local dielectric anisotropy occurs naturally, and should be expected to play a role [24]. Thus, it is also interesting to see what happens to the NDEDA as one takes into account the local dielectric anisotropy. The resultant anisotropic NDEDA will help to investigate the AC electrokinetic phenomena of biological cells [25]. Work along this direction is in progress.

To sum up, we put forth an NDEDA and a first-principles approach for investigating the optical responses of nonlinear graded spherical particles. The excellent agreement between the two methods has been shown. As an application, we applied the NDEDA to discuss the surface plasma resonance effect on the effective linear and nonlinear optical properties like the optical absorption, the optical nonlinearity enhancement, and the figure of merit. It is found that the dielectric gradation profile can be used to control the surface plasma resonance and achieve the large figure of merit in the high-frequency region, where the optical absorption is quite small.

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FIGURES

FIG. 1. The effective linear dielectric constant $\epsilon_e$ versus $A$ for the power-law dielectric gradation profile $\epsilon(r) = A(r/a)^n$ in the dilute limit $f = 0.05$. Lines: numerical results from the NDEDA [Eq. (8)]; Symbols: exact results [Eq. (18)].

FIG. 2. The effective third-order nonlinear susceptibility $\chi_e$ versus $A$ for power-law dielectric-constant gradation profile $\epsilon(r) = A(r/a)^n$ and linear nonlinear-susceptibility gradation profile $\chi(r) = k_1 + k_2 \cdot r/a$ with (a) $k_1 = 1$ and $k_2 = 1$, and (b) $k_1 = 2$ and $k_2 = 3$. Lines: numerical results from the NDEDA [Eqs. (8) and (13)]; Symbols: exact results [Eq. (19)].

FIG. 3. Same as Fig.2, but for power-law nonlinear-susceptibility gradation profile $\chi(r) = k_1(r/a)^{k_2}$.

FIG. 4. (a) The linear optical absorption $\text{Im}(\epsilon_e)$, (b) the enhancement of the third-order optical nonlinearity $|\chi_e|/\chi_1$, and (c) the figure of merit $\equiv |\chi_e|/\text{Im}(\epsilon_e)$ versus the incident angular frequency $\omega/\omega_p$ for dielectric-constant gradation profile $\epsilon(r) = 1 - \omega_p^2(r)/[\omega(\omega + i\gamma(r))]$ with $\omega_p(r) = \omega_p(1 - k_\omega \cdot r/a)$ and $\gamma(r) = 0.01\omega_p$. Parameters: $\epsilon_2 = 1.77$ and $f = 0.05$.

FIG. 5. Same as Fig.4, but with $\omega_p(r) = \omega_p$ and $\gamma(r) = \gamma(\infty) + k_\gamma/(r/a)$ for $\gamma(\infty) = 0.01\omega_p$.
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Fig. 2. /Gao, Huang and Yu
Fig. 3. /Gao, Huang and Yu
Fig. 4. /Gao, Huang and Yu
Fig. 5. /Gao, Huang and Yu