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Effective nonlinear optical properties of composite media of graded spherical particles

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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 plasmon 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.[8–14] 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[15] and multishell model,[16] 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 a very small volume fraction of 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 Sec. II, we describe the model and define briefly the effective linear dielectric constant and third-order nonlinear susceptibility. In Sec. 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 Sec. 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 Sec. V. Finally, some conclusion and discussion is shown in Sec. VI.

II. MODEL AND DEFINITION OF EFFECTIVE LINEAR AND NONLINEAR RESPONSES

Let us consider a nonlinear composite system, in which identical graded spherical inclusions with radius a, are randomly embedded in a linear host medium of dielectric constant ϵ_2. The local constitutive relation between the displacement $\mathbf{D}$ and the electric field $\mathbf{E}$ inside the graded particle is given by

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

where $\epsilon(r)$ and $\chi(r)$ are the linear dielectric constant and third-order nonlinear susceptibility, respectively. Note both $\epsilon(r)$ and $\chi(r)$ are radial functions. Here we assume that the weak nonlinearity condition is satisfied.[8] In other words, the contribution of the second (nonlinear) part $[\chi(r)|\mathbf{E}|^2]$ 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 quasistatic approximation, under which the whole composite medium can be regarded as an effective homogeneous one with effective linear dielectric constant ϵ_e and effective third-order nonlinear susceptibility χ_e. To show the definitions of ϵ_e and χ_e, we have[8]

$$\langle \mathbf{D}\rangle = \epsilon_e \mathbf{E}_0 + \chi_e |\mathbf{E}_0|^2 \mathbf{E}_0, \tag{2}$$

where $\langle \cdots \rangle$ represents the spatial average, and $\mathbf{E}_0 = E_0 \mathbf{e}_z$ is the external applied field along z axis.

The effective linear dielectric constant ϵ_e is given by

$$\epsilon_e \mathbf{E}_0 = \frac{1}{V}\int_V \epsilon_i \mathbf{E}_{\text{lin,i}} dV = f\langle \epsilon(r)\mathbf{E}_{\text{lin,1}}\rangle + (1-f)\epsilon_2 \langle \mathbf{E}_{\text{lin,2}}\rangle, \tag{3}$$

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, χ_e can then be written as[8,17]

$$\chi_e \mathbf{E}_0^2 \mathbf{E}_0^2 = \frac{1}{V}\int_V \chi_i |\mathbf{E}|^2_{\text{lin,i}} \mathbf{E}^2_{\text{lin,i}} dV = \frac{1}{V}\int_{\Omega_i} \chi(r) |\mathbf{E}|^2_{\text{lin,1}} \mathbf{E}^2_{\text{lin,1}} dV$$
$$= f\langle \chi(r) |\mathbf{E}|^2_{\text{lin,1}} \mathbf{E}^2_{\text{lin,1}}\rangle. \tag{4}$$

In the following section, we will develop a NDEDA (nonlinear differential effective dipole approximation), in an attempt to derive the equivalent linear dielectric constant $\overline{\epsilon}(a)$ and third-order nonlinear susceptibility $\overline{\chi}(a)$ 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 multishell construction. 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 $\overline{\epsilon}(r)$ and $\overline{\chi}(r)$. Here the homogeneous 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 $\overline{\epsilon}(r)$, and nonlinear susceptibility $\overline{\chi}(r)$, and a shell with outermost radius $r+\mathrm{d}r$, linear dielectric constant $\epsilon(r)$, and nonlinear susceptibility $\chi(r)$. Since these coated inclusions with a very small volume fraction are randomly embedded in a linear host medium, under the quasistatic approximation, we can readily obtain the linear electric potentials in the core, shell and host medium by solving the Laplace equation[18]

$$\phi_c = -E_0 A R\cos\theta, \quad R<r,$$
$$\phi_s = -E_0\left(BR - \frac{Cr^3}{R^2}\right)\cos\theta, \quad r<R<r+dr,$$
$$\phi_h = -E_0\left(R - \frac{D(r+dr)^3}{R^2}\right)\cos\theta, \quad R>r+\mathrm{d}r, \tag{5}$$

where

$$A = \frac{9\epsilon_2 \epsilon(r)}{Q}, \quad B = \frac{3\epsilon_2[\overline{\epsilon}(r)+2\epsilon(r)]}{Q},$$

$$C = \frac{3\epsilon_2[\overline{\epsilon}(r)-\epsilon(r)]}{Q},$$

$$D = \frac{[\epsilon(r)-\epsilon_2][\overline{\epsilon}(r)+2\epsilon(r)] + \lambda[\epsilon_2+2\epsilon(r)][\overline{\epsilon}(r)-\epsilon(r)]}{Q},$$

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

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

The effective (overall) linear dielectric constant of the system is determined by the dilute-limit expression[19]

$$\epsilon_e = \epsilon_2 + 3p\epsilon_2 D, \tag{6}$$

where p is the volume fraction of graded particles with radius r. The equivalent dielectric constant $\overline{\epsilon}(r+dr)$ for the graded particles with radius $r+dr$ can be obtained self-consistently by the vanishing of the dipole factor D by replacing ϵ_2 with $\overline{\epsilon}(r+dr)$. Taking the limit $dr \to 0$ and keeping to the first order in dr, we obtain

$$\overline{\epsilon}(r+dr) = \epsilon(r) + 3\epsilon(r)\lambda \frac{\overline{\epsilon}(r)-\epsilon(r)}{\overline{\epsilon}(r)(1-\lambda)+\epsilon(r)(2+\lambda)}$$
$$= \overline{\epsilon}(r) - \frac{\overline{\epsilon}(r)-\epsilon(r)}{r}\left[3 + \frac{\overline{\epsilon}(r)-\epsilon(r)}{\epsilon(r)}\right]dr. \tag{7}$$

Thus, we have the differential equation for the equivalent dielectric constant $\overline{\epsilon}(r)$ as[6]

$$\frac{d\overline{\epsilon}(r)}{dr} = \frac{[\epsilon(r)-\overline{\epsilon}(r)][\overline{\epsilon}(r)+2\epsilon(r)]}{r\epsilon(r)}. \tag{8}$$

Note that Eq. (8) is just the Tartar formula, derived for assemblages of spheres with varying radial and tangential conductivity.[20]

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

$$\overline{\chi}(r+dr)\frac{\langle|\mathbf{E}|^2\mathbf{E}^2\rangle_{R\leq r+dr}}{|\mathbf{E}_0|^2\mathbf{E}_0^2} = \lambda\overline{\chi}(r)\frac{\langle|\mathbf{E}|^2\mathbf{E}^2\rangle_{R\leq r}}{|\mathbf{E}_0|^2\mathbf{E}_0^2}+(1-\lambda)\frac{\langle\chi(r)|\mathbf{E}|^2\mathbf{E}^2\rangle_{r<R\leq r+dr}}{|\mathbf{E}_0|^2\mathbf{E}_0^2}. \tag{9}$$

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

$$\begin{aligned}\overline{\chi}(r+dr)\frac{\langle|\mathbf{E}|^2\mathbf{E}^2\rangle_{R\leq r+dr}}{|\mathbf{E}_0|^2\mathbf{E}_0^2} &= \overline{\chi}(r+dr)\left|\frac{3\epsilon_2}{\overline{\epsilon}(r+dr)+2\epsilon_2}\right|^2\left(\frac{3\epsilon_2}{\overline{\epsilon}(r+dr)+2\epsilon_2}\right)^2 \\ &= \overline{\chi}(r)|K|^2K^2 - dr\,\overline{\chi}(r)|K|^2K^2\left[\frac{3d\overline{\epsilon}(r)/dr}{2\epsilon_2+\overline{\epsilon}(r)} + \left(\frac{d\overline{\epsilon}(r)/dr}{2\epsilon_2+\overline{\epsilon}(r)}\right)^*\right] + |K|^2K^2\frac{d\overline{\chi}(r)}{dr}dr,\end{aligned} \tag{10}$$

with $K=(3\epsilon_2)/[\overline{\epsilon}(r)+2\epsilon_2]$. The first part of the right-hand side of Eq. (9) is written as

$$\lambda\frac{\overline{\chi}(r)\langle|\mathbf{E}|^2\mathbf{E}^2\rangle_{R\leq r}}{|\mathbf{E}_0|^2\mathbf{E}_0^2} = \overline{\chi}(r)|K|^2K^2\left[1+(6y+2y^*-3)\frac{\mathrm{d}r}{r}\right], \tag{11}$$

where

$$y=\frac{[\epsilon(r)-\epsilon_2][\overline{\epsilon}(r)-\epsilon(r)]}{\epsilon(r)[\overline{\epsilon}(r)+2\epsilon_2]}.$$

The second part of the right-hand side of Eq. (9) has the form[19]

$$\begin{aligned}(1-\lambda)\frac{\langle\chi(r)|\mathbf{E}|^2\mathbf{E}^2\rangle_{r<R\leq r+dr}}{|\mathbf{E}_0|^2\mathbf{E}_0^2} &= \frac{3\chi(r)}{5r}dr|z|^2z^2(5+18x^2+18|x|^2 \\ &\quad +4x^3+12x|x|^2+24|x|^2x^2),\end{aligned} \tag{12}$$

where

$$x=\frac{\overline{\epsilon}(r)-\epsilon(r)}{\overline{\epsilon}(r)+2\epsilon(r)} \quad \text{and} \quad z=\frac{\epsilon_2[\overline{\epsilon}(r)+2\epsilon(r)]}{\epsilon(r)[\overline{\epsilon}(r)+2\epsilon_2]}.$$

Substituting Eqs. (10)–(12) into Eq. (9), we have a differential equation for the equivalent nonlinear susceptibility $\overline{\chi}(r)$, namely,

$$\begin{aligned}\frac{d\overline{\chi}(r)}{dr} &= \overline{\chi}(r)\left[\frac{3d\overline{\epsilon}(r)/dr}{2\epsilon_2+\overline{\epsilon}(r)} + \left(\frac{d\overline{\epsilon}(r)/dr}{2\epsilon_2+\overline{\epsilon}(r)}\right)^*\right] \\ &\quad + \overline{\chi}(r)\left(\frac{6y+2y^*-3}{r}\right) \\ &\quad + \frac{3\chi(r)}{5r}\left|\frac{\overline{\epsilon}(r)+2\epsilon(r)}{3\epsilon(r)}\right|^2\left(\frac{\overline{\epsilon}(r)+2\epsilon(r)}{3\epsilon(r)}\right)^2 \\ &\quad \times(5+18x^2+18|x|^2+4x^3+12x|x|^2+24|x|^2x^2).\end{aligned} \tag{13}$$

So far, the equivalent $\overline{\epsilon}(r)$ and $\overline{\chi}(r)$ 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 $\overline{\chi}(r)$ 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 $\overline{\epsilon}(r)=\epsilon_1$ and $\overline{\chi}(r)=\chi_1$.

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

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

and

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

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]

$$\phi_i(r)=-\xi_1E_0r^s\cos\theta, \quad r<a,$$

$$\phi_h(r)=-E_0r\cos\theta+\frac{\xi_2}{r^2}E_0\cos\theta, \quad r>a, \tag{16}$$

where the coefficients ξ_1 and ξ_2 have the form

$$\xi_1=\frac{3a^{1-s}\epsilon_2}{sA+2\epsilon_2} \quad \text{and} \quad \xi_2=\frac{sA-\epsilon_2}{sA+2\epsilon_2}a^3,$$

and s is given by

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

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

$$\mathbf{E}_i=\xi_1 E_0 r^{s-1}(s\cos\theta\mathbf{e}_r-\sin\theta\mathbf{e}_\theta)=\xi_1 E_0 r^{s-1}\{(s-1)\cos\theta\times\sin\theta\cos\phi\mathbf{e}_x+(s-1)\cos\theta\sin\theta\sin\phi\mathbf{e}_y+[(s-1)\cos^2\theta+1]\mathbf{e}_z\},\tag{17}$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are unix vectors in spherical coordinates and in Cartesian coordinates. In the dilute limit, from Eq. (3), we can obtain the effective linear dielectric constant as follows

$$\epsilon_e=\epsilon_2+\frac{1}{VE_0}\int_{\Omega_i}[A(r/a)^n-\epsilon_2]\mathbf{e}_z\cdot\mathbf{E}_i dV=\epsilon_2+3\epsilon_2 f\frac{2+s}{sA+2\epsilon_2}\left(\frac{A}{2+n+s}-\frac{\epsilon_2}{2+s}\right).\tag{18}$$

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

$$\chi_e=\frac{1}{V}\int_{\Omega_i}\chi(r)|\xi_1|^2\xi_1^2(s^2\cos^2\theta+\sin^2\theta)^2 r^{4s-2}\sin\theta dr d\theta d\phi=\frac{f}{5a^3}|\xi_1|^2\xi_1^2(8+4s+3s^4)\int_0^a\chi(r)r^{4s-2}dr.\tag{19}$$

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

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

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

$$\chi_e=\frac{f}{5}\left|\frac{3\epsilon_2}{sA+2\epsilon_2}\right|^2\left(\frac{3\epsilon_2}{sA+2\epsilon_2}\right)^2 k_1\left(\frac{8+4s^2+3s^4}{k_2-1+4s}\right).\tag{21}$$

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 $\chi(r)=k_1+k_2 r/a$, 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.

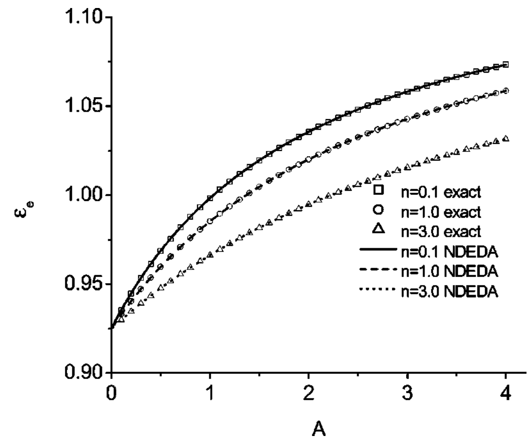

FIG. 1. The effective linear dielectric constant ϵ_e vs A for the power-law dielectric gradation profile $\epsilon(r)=A(r/a)^n$ in the dilute limit $f=0.05$. Lines: numerical results from the NDEDA [Eq. (8)]; symbols: exact results [Eq. (18)].

In Fig. 1, the effective linear dielectric constant (ϵ_e) is plotted as a function of A for various indices n. It is shown that ϵ_e exhibits a monotonic increase for increasing A (and decreasing n). This can be understood by using the equivalent dielectric constant $\overline{\epsilon(r=a)}$ 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 (χ_e) is plotted as a function of A for the linear gradation profile $\chi(r)=k_1+k_2 r/a$ (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 χ_e. In addition, increasing n leads generally to increasing χ_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 plasmon resonance effect on the metal-dielectric composite. We adopt the Drude-like dielectric constant for graded metal particles, namely,

$$\epsilon(r)=1-\frac{\omega_p^2(r)}{\omega[\omega+\mathrm{i}\gamma(r)]},\tag{22}$$

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

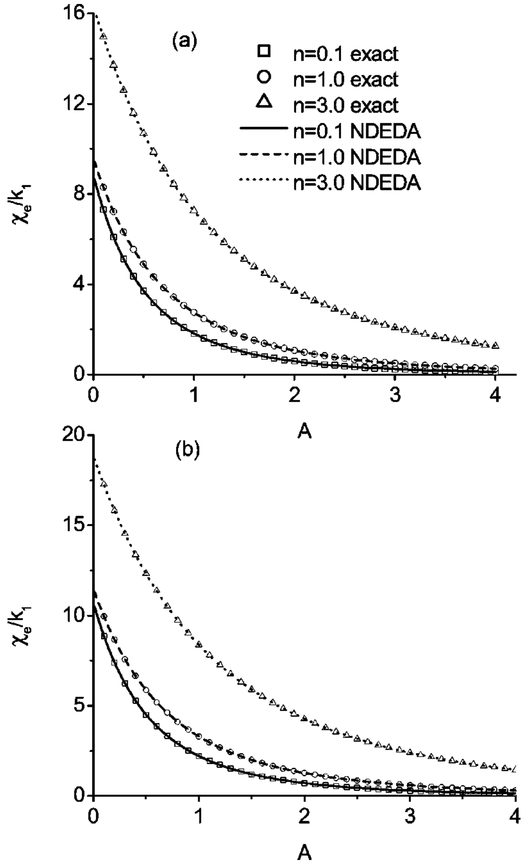

FIG. 2. The effective third-order nonlinear susceptibility χ_e vs A for power-law dielectric-constant gradation profile $\epsilon(r)=A(r/a)^n$ and linear nonlinear-susceptibility gradation profile $\chi(r)=k_1+k_2r/a$ with (a) $k_1=1$ and $k_2=1$, and (b) $k_1=2$ and $k_2=3$. Lines: numerical results from the NDEDA [Eqs. (8) and (13)]; symbols: exact results [Eq. (19)].

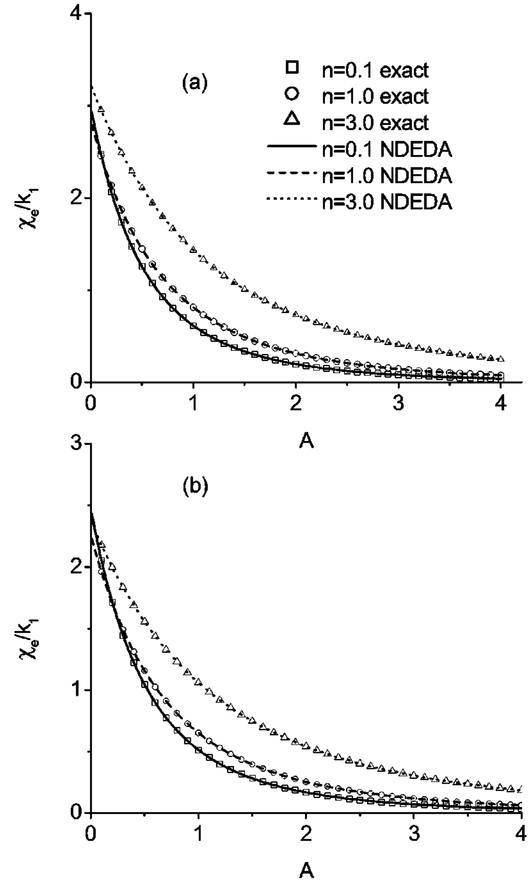

FIG. 3. Same as Fig. 2, but for power-law nonlinear-susceptibility gradation profile $\chi(r)=k_1(r/a)^{k_2}$.

$$\omega_p(r)=\omega_p\left(1-k_\omega\frac{r}{a}\right),\quad r<a. \tag{23}$$

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.[21] For small particles, we have the radius dependent $\gamma(r)$ as[22]

$$\gamma(r)=\gamma(\infty)+\frac{k_\gamma}{r/a},\quad r<a, \tag{24}$$

where $\gamma(\infty)$ stands for the damping coefficient in the bulk material. Here k_γ 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. 4, we plot the optical absorption $[\sim\mathrm{Im}(\epsilon_e)]$, the modulus of the effective third-order optical nonlinearity enhancement ($|\chi_e|/\chi_1$) and the figure of merit ($|\chi_e|/\mathrm{Im}(\epsilon_e)$) versus the incident angular frequency ω. For the case of the homogeneous particles, i.e., $k_\omega=0$, there is a single sharp peak at $\omega\approx 0.5\omega_p$, corresponding to the surface plasmon resonance, as expected. However, for the case of the graded particles, i.e., $k_\omega\neq 0$, besides a sharp peak, a broad continuous resonant band in the high-frequency region is apparently observed. The position of the sharp peak can be estimated from the resonant condition $\mathrm{Re}[\overline{\epsilon(r=a)}]+2\epsilon_2=0$, while the broad continuous spectrum is indeed a salient result of the gradation profile. More exactly, the broad spectrum results from the effect of the radius-dependent plasma frequency. In Ref. 15, we found that, when the shell model is taken into account, a broad continuous spectrum should be expected to occur around the large pole in the spectral density function. In fact, the graded particles under consideration can be regarded as a certain limit of multishells, which thus should yield the broader spectra in $\mathrm{Im}(\epsilon_e)$, $|\chi_e|/\chi_1$ as well as $|\chi_e|/\mathrm{Im}(\epsilon_e)$. In addition, we note that increasing k_ω makes both the surface plasmon frequency and the center of the resonant bands 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 *weak* optical absorption. Thus, we believe that graded particles 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

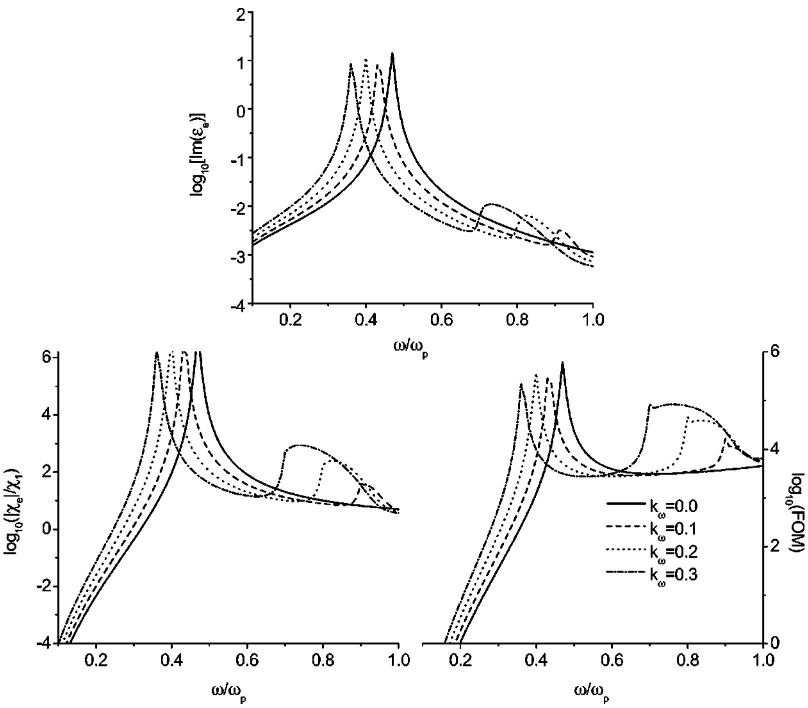

FIG. 4. (a) The linear optical absorption $\mathrm{Im}(\epsilon_e)$, (b) the enhancement of the third-order optical nonlinearity $|\chi_e|/\chi_1$, and (c) the figure of merit $\equiv|\chi_e|/\mathrm{Im}(\epsilon_e)$ vs the incident angular frequency ω/ω_p for dielectric-constant gradation profile $\epsilon(r)=1-\omega_p^2(r)/[\omega(\omega+i\gamma(r))]$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

optical property in Fig. 5. As evident from the results, the variation of k_γ plays an important role in the magnitude of the effective optical properties, particularly at the surface plasmon 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.

In this work, the NDEDA was derived for the composite

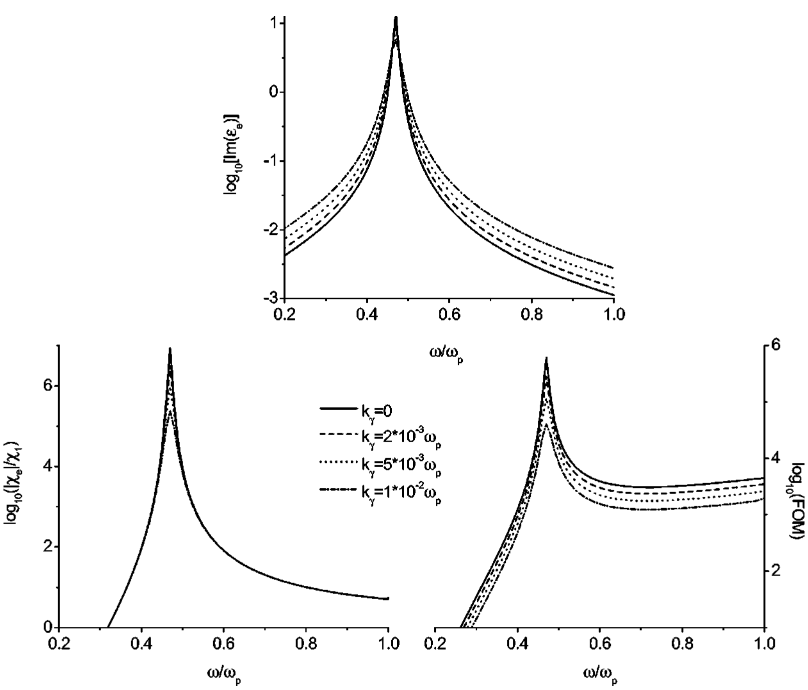

FIG. 5. Same as Fig. 4, but with $\omega_p(r)=\omega_p$ and $\gamma(r)=\gamma(\infty)+k_\gamma/(r/a)$ for $\gamma(\infty)=0.01\omega_p$.

containing the nonlinear graded inclusions in a linear host. Interestingly, it can be readily generalized to the composite system where the graded inclusions and the host are both nonlinear.[23] In this situation, the effective third-order nonlinear response can be written as,[24,25]

$$\chi_e = f\overline{\chi}(r=a)\left|\frac{3\epsilon_2}{\overline{\epsilon}(r=a)+2\epsilon_2}\right|^2\left(\frac{3\epsilon_2}{\overline{\epsilon}(r=a)+2\epsilon_2}\right)^2 + \chi_2(1-f)+\chi_2 f\left(3\beta+\beta^*+\frac{18}{5}\beta^2+\frac{18}{5}|\beta|^2 + \frac{6}{5}|\beta|^2\beta+\frac{2}{5}\beta^3+\frac{8}{5}|\beta|^2\beta^2\right), \tag{25}$$

where $\beta \equiv [\overline{\epsilon}(r=a)-\epsilon_2]/[\overline{\epsilon}(r=a)+2\epsilon_2]$ and χ_2 is the third-order nonlinear susceptibility of the host medium. As a matter of fact, for this purpose, the perturbation method can also be adopted.[26]

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.[27] Therefore, it is of particular interest to generalize the NDEDA for treating the case of high volume fractions.

It is also instructive to develop the first-principles approach to weakly nonlinear graded composites. The perturbation approach[28] in weakly nonlinear composites is just suitable for this problem. Moreover, with the aim of the variational approach,[29] the NDEDA may be applied to the cases of strong nonlinearity, where the linear part $[\epsilon(r)]$ in Eq. (1) vanishes. On the other hand, based on the self-consistent mean-field approximation,[30] the applicability of NDEDA to more general cases, where linear $[\epsilon(r)]$ and nonlinear $[\chi(r)|\mathbf{E}|^2]$ parts can be comparable, may be also possible.

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.[31] 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.[32] 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 plasmon 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 plasmon resonance and achieve the large figure of merit in the high-frequency region, where the optical absorption is quite small.

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