Second-harmonic generation in graded metal–dielectric films of anisotropic particles

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Abstract

We investigate theoretically the effective second-harmonic generation (SHG) susceptibility in graded films of metal–dielectric random composites with anisotropically shaped particles by invoking the local field effects. Using numerical examples, we demonstrate that in the presence of gradation profiles and/or shape effects, graded metal–dielectric films could be used as novel optical materials for producing a broad structure in both the linear and nonlinear (SHG) response and with an enhancement in the nonlinear response.

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1. Introduction

Nonlinear optical materials with an appreciable nonlinear susceptibility or optimal figure of merit (FOM) [1–3] are of importance in industrial applications such as nonlinear optical switching devices in photonics and real-time coherent optical signal processors. In general, many applications of nonlinear optics that have been demonstrated under controlled laboratory conditions could become practical for technological uses if such materials were available. Much work have been done on how to achieve a substantial nonlinear optical response or/and optimal FOM in bulk metal–dielectric composites, by invoking the surface–plasmon resonance [4,5] and by incorporating structural effects [6–8]. For nonlinear phenomena in Kerr composites, the nonlinear alternating current responses have been investigated [9–12]. For nonlinear effects other than the Kerr effect, Hui and Stroud [13]...
derived general expressions for the effective susceptibility for the second-harmonic generation (SHG) in a binary composite of random dielectrics. Recently, these authors have also studied the thickness dependence of the effective SHG susceptibility in films of random dielectrics [14] and the enhancement in the SHG in dilute composites of coated small particles [15].

Graded materials with various functionalities appear in nature and in fabricated materials. These materials have many applications as the gradation profile provides an additional means of controlling the physical properties. In other words, graded materials could have quite different physical properties from homogeneous materials [16–22]. To achieve desired optical responses, the technique of gradation is expected to be useful for a variety of optical materials, e.g., metal–dielectric composites and negative-refractive-index metamaterials [23,24]. In particular, graded thin films often possess different optical properties, when compared with a film processing the same properties at different locations along the growth direction. For example, a large enhancement in nonlinear optical responses was found in a composite of alternating, sub-wavelength-thick layers of titanium dioxide and conjugated polymer [7], which can be regarded as a graded material. It has also been observed that compositionally graded barium strontium titanate thin films have better electric properties than a single-layer barium strontium titanate film with the same composition [25].

Crucial elements for controlling the linear and nonlinear optical properties of metal–dielectric composites include the micro-structure of the composite, particle shape, and the properties of the constituents. For anisotropically shaped metallic nanoparticles, the resonant plasmon bands split for orientations along the major and minor axes. In the case of a large size aspect ratio, the plasmon bands may shift downward in frequency into the infrared, thus enabling the possible use of metal nanostructures in telecommunication applications. When compared with spherically shaped particles, anisotropically shaped metallic particles show reduced plasmon relaxation times [26] as well as enhanced nonlinear responses [27], and may thus be used as building blocks in a variety of optical devices. Experimentally, techniques have been developed to fabricate rod-shaped metallic nanoparticles by using lithographic means [28] or anisotropic growth. Recently, it has been demonstrated that ion irradiation in the energy range of mega-electron-volt (MeV) can also be used to modify the shape of nanoparticles [29]. This ion-beam-induced anisotropic deformation effect is known to occur not only in a wide range of amorphous materials [30], but also in crystalline materials including metals [31]. With this advancement in experimental techniques, samples of spheroidal metallic particles randomly dispersed in a dielectric host can readily be prepared.

To achieve an enhanced and controllable SHG in functional optical materials is still a challenging task (see Refs. [21,32] and references therein). In this Letter, we investigate the effects of gradation and/or particle shape on the SHG response in graded metal–dielectric films. In these films, the volume fraction of the anisotropically shaped metallic particles varies in the direction perpendicular to the film, i.e., along the growth direction of the film. The Letter is organized as follows. In Section 2, we derive an expression of the effective SHG susceptibility of a graded metal–dielectric film consisting of anisotropically shaped metallic particles. In Section 3, results of model calculations are presented for different gradation profiles and shapes. The Letter ends with a discussion and conclusion in Section 4.

2. Formalism

We consider a graded metal–dielectric composite film of thickness $L$, with the gradation profile in the direction (z-direction) perpendicular to the film (Fig. 1). If one considers quadratic nonlinearities only, the local constitutive relation between the displacement field $D(z)$ and the electric field $E(z)$ in the static case is given by [14,15]

$$D_i(z) = \sum_{j} \epsilon_{ij}(z)E_j(z) + \sum_{jk} \chi_{ijk}(z)E_j(z)E_k(z),$$

where $D_i(z)$ and $E_i(z)$ are the $i$th component of $\mathbf{D}(z)$ and $\mathbf{E}(z)$, respectively, and $\chi_{ijk}$ the SHG susceptibility. Here $\epsilon_{ij}(z) = \epsilon(z)\delta_{ij}$ denotes the linear dielectric constant, which is assumed for simplicity to be isotropic. Both $\epsilon(z)$ and $\chi_{ijk}(z)$ are functions of $z$, as a result of the gradation profile in the z-direction.
Fig. 1. Schematic graph to show the geometry of a graded metal–dielectric composite film with a variation of volume fraction of (a) prolate and (b) oblate spheroidal metallic particles along $z$-axis perpendicular to the film. The electric field $E$ is parallel to the gradient along $z$-axis.

If a monochromatic external field is applied, the nonlinearity in the system will generally generate local potentials and fields at all harmonic frequencies. For a finite frequency external electric field of the form

$$E_0 = E_0(\omega)e^{-i\omega t} + c.c.,$$

the effective SHG susceptibility $\chi_2(\omega)$ can be extracted by considering the volume average of the displacement field at the frequency $2\omega$ in the inhomogeneous medium [13–15,21].

Let $p(z)$ be the volume fraction of the metallic component in the graded film. To calculate $\epsilon(z, \omega)$, we invoke the well-known Maxwell–Garnett approximation [33]

$$\begin{align*}
\epsilon(z, \omega) &= \epsilon_2 \\
\epsilon(z, \omega) &= \frac{\epsilon(z, \omega) - \epsilon_2}{L_z \epsilon_2 + (1 - L_z) \epsilon_1} = p(z) \frac{\epsilon_1(\omega) - \epsilon_2}{L_z \epsilon_1(\omega) + (1 - L_z) \epsilon_2},
\end{align*}$$

where $\epsilon_1(\omega)$ and $\epsilon_2$ are the linear dielectric constants of the metallic and dielectric components, respectively. Here, $L_z$ is the depolarization factor describing the anisotropy of the metallic particles along the $z$-axis, with $0 < L_z < 1/3$ (or $1/3 < L_z < 1$) denoting prolate (or oblate) spheroids and $L_z = 1/3$ for spherical particles [16]. It is worth noting that prolate spheroidal particles can more easily be fabricated than oblate spheroidal particles in experiments using the method of ion irradiation (see, e.g., Ref. [31]).

For completeness, we discuss both prolate and oblate spheroidal particles (Fig. 2). Implicit in Eq. (3) is the assumption that the major axes of the metallic particles are aligned perpendicular to the film. Experimentally, prolate spheroidal metallic particles can be made highly oriented along the direction of irradiated ions [31].

The dielectric function $\epsilon_1(\omega)$ of the metallic component is taken to be the Drude form

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)},$$

where $\omega_p$ denotes the plasma frequency and $\gamma$ the relaxation rate. For a $z$-dependent volume fraction profile $p(z)$, we can make use of the equivalent capacitance for capacitors in series to evaluate the effective perpendicular linear dielectric response $\bar{\epsilon}(\omega)$ at a given frequency, i.e.,

$$\frac{1}{\bar{\epsilon}(\omega)} = \frac{1}{L} \int_0^L dz \frac{1}{\epsilon(z, \omega)}.$$

The treatment of the effective linear response is analogous to the effective medium approximation for the thermal properties of graded films [20].

The calculation of the effective nonlinear optical response proceeds by applying the expressions derived in Ref. [13]. The effective SHG susceptibility $\chi_2(\omega)$ for the slice of the system at position $z$ is given by [14,15]

$$\bar{\chi}_2(\omega) = p(z) \chi_2 \alpha(z, 2\omega) [\alpha(z, \omega)]^2,$$

where $\alpha(z, \omega)$ denotes the local-field factor in a linear inhomogeneous system [13] which, for consistency with Eq. (3) in getting $\epsilon(z, \omega)$, should also be determined by using the Maxwell–Garnett approach. The result is

$$\alpha(z, \omega) = \frac{\epsilon_2}{\epsilon_2 [1 - L_z (1 - p(z))] + \epsilon_1(\omega) L_z (1 - p(z))}.$$

In Eq. (6), $\chi_2(\omega)$ is the intrinsic SHG susceptibility of the metallic component. For simplicity, we assumed that the dielectric host is linear. The effective SHG susceptibility $\chi_2(\omega)$ of the whole film can then be evaluated by a one-dimensional integral over the film thickness
to give
\[ \tilde{\chi}_{2\omega} = \frac{1}{L} \int_0^L dz \tilde{\chi}_{2\omega}(z) \left( \frac{E(z, 2\omega)}{E_0} \right) \left( \frac{\tilde{E}(z, \omega)}{E_0} \right)^2, \]  
(8)

where \( E(z, \omega) \) denotes the volume average of the electric field within a layer at position \( z \).

By virtue of the continuity of electric displacement, there is a relation
\[ \epsilon(z, \omega) = \tilde{\epsilon}(\omega) = \epsilon(\omega). \]  
(9)

Thus, we obtain
\[ \tilde{\chi}_{2\omega} = \frac{1}{L} \int_0^L dz \tilde{\chi}_{2\omega}(z) \left( \frac{\tilde{\epsilon}(2\omega)}{\epsilon(z, \omega)} \right)^2, \]  
(10)

Eq. (10), coupled with Eqs. (3) and (5), gives a compact expression for the effective SHG susceptibility in graded films.

3. Numerical results

For illustration, we take a model profile of metallic volume fraction of the form
\[ p(z) = az^m, \]  
(11)

where \( a \) and \( m \) are constants tuning the profile. Without loss of generality, the thickness \( L \) is set to unity, i.e., thickness is measured in units of \( L \). Given values of \( m \) and \( a \) corresponding to a certain volume fraction \( p \) of metallic component in the film,
\[ p = \frac{1}{L} \int_0^L p(z) \, dz. \]  
(12)

For a given profile \( p(z) \), if we randomly disperse the same amount of anisotropic metallic component in a film of thickness \( L \), the effective SHG susceptibility \( \chi_0 \) for the random film would be \([14,15]\)
\[ \chi_0 = p \chi_{2\omega} \alpha(2\omega) [\alpha(\omega)]^2, \]  
(13)

where the local-field factor \( \alpha(\omega) \) is given by an expression similar to Eq. (7) as
\[ \alpha(\omega) = \frac{\epsilon_2}{\epsilon_2 [1 - L_z (1 - p)] + \epsilon_1(\omega) L_z (1 - p)}. \]  
(14)

By comparing the effective SHG susceptibility \( \tilde{\chi}_{2\omega} \) with \( \chi_0 \) (see Fig. 3), we can see whether a graded film gives an enhanced SHG response, when compared to a nongraded film of random composite with the same volume fraction of metallic component.

We have carried out model numerical calculations to investigate the effects on the local field factors in Eq. (6) due to the gradation profile, the metallic particle shape, and the difference in the linear dielectric response between the two constituents. Fig. 2 shows the effects of different degrees of anisotropy as specified by different values of the depolarization factor \( L_z \). Fig. 2 gives the real and imaginary parts of the effective linear dielectric constant \( \epsilon(\omega) \) (Fig. 2(a) and (b)), and the real and imaginary parts of the effective SHG susceptibility \( \tilde{\chi}_{2\omega} \) (Fig. 2(c) and (d)) as a function of frequency \( \omega/\omega_p \). Also shown is the modulus of \( \tilde{\chi}_{2\omega}/\chi_{2\omega} \) (see Fig. 2(e)). For Fig. 2 (and Fig. 3), we take the parameters \( a = 0.8 \) and \( m = 1 \), which correspond to the total volume fraction \( p = 0.4 \) according to Eq. (12). As \( L_z \) decreases, i.e., as the shape of the particles changes from oblate spheroid, to sphere, and then to prolate spheroid, the plasmon band becomes broader, and also shifts to lower frequencies, see Fig. 2(b). In Fig. 2(c)–(e), \( \tilde{\chi}_{2\omega} \) is normalized by the intrinsic SHG susceptibility of the metallic component \( \chi_0 \), which is assumed to be a real and positive frequency-independent constant. In Fig. 2(c)–(e), there exists a frequency range in which a significantly enhanced SHG susceptibility results, when compared with \( \chi_0 \). As \( L_z \) decreases, the frequency range becomes narrower and red-shifted to lower frequencies (see Fig. 2(c)–(e)).

It is also illustrative to compare the results in the presence of a gradation profile with that of a random composite film consisting of the same amount of metallic (nonlinear) component. In Fig. 3, we show the results for \( \tilde{\chi}_{2\omega}/\chi_0 \), where \( \chi_0 \) is given by Eq. (13). The results indicate that a gradation profile may not always enhance the SHG response. Generally speaking, one has to carefully make sure of the dielectric contrast, together with composition and gradation profiles, to achieve SHG enhancement in certain ranges of frequencies.

To further investigate the effects of a gradation profile, we consider a fixed volume fraction \( p \) of the nonlinear component. For a profile of the form \( p(z) = az^m \), Eq. (12) implies that the parameters \( a \) and \( m \)
Fig. 2. (a) $\text{Re} \{\tilde{\epsilon}(\omega)\}$, (b) $\text{Im} \{\tilde{\epsilon}(\omega)\}$, (c) $\text{Re} \{\tilde{\chi}_2(\omega)/\chi_2^0\}$, (d) $\text{Im} \{\tilde{\chi}_2(\omega)/\chi_2^0\}$, and (e) modulus of $\tilde{\chi}_2(\omega)/\chi_2^0$, versus the normalized incident angular frequency $\omega/\omega_p$ for layer metal profile $p(z) = az^m$, for different $L_z$. Here $|\cdots|$ denotes the absolute value or modulus of $\cdots$. Parameters: $a = 0.8$, $m = 1$, $\gamma/\omega_p = 0.01$, and $\epsilon_2 = (3/2)^2$.

Fig. 3. Same as Fig. 2(c)–(e), respectively, but (a) $\text{Re} \{\tilde{\chi}_2(\omega)/\chi_2^0\}$, (b) $\text{Im} \{\tilde{\chi}_2(\omega)/\chi_2^0\}$, and (c) modulus of $\tilde{\chi}_2(\omega)/\chi_2^0$.

Fig. 4. Shows the results at the fixed frequency of $\omega/\omega_p = 0.2$ for different profiles characterized by the parameter $m$, for four different values of volume fraction $p = 0.1, 0.2, 0.3$, and 0.4. The linear responses can be enhanced to different extent with a gradation profile (see Fig. 4(a) and (b)). The imaginary part of the linear dielectric response (Fig. 4(b)) shows a broad structure with frequency with a broad peak at frequencies at which the real part shows a sharp drop (Fig. 4(a)), expect for the system with the lowest concentration of nonlinear component. Fig. 4(c)–(e)
Fig. 4. Same as Fig. 2, but versus $m$ (dimensionless) for different total volume fraction $p$. Parameters: $L_z = 0.1$, $\omega/\omega_p = 0.2$, $\gamma/\omega_p = 0.01$, and $\epsilon_2 = (3/2)^2$.

shows that the SHG responses are highly sensitive to the gradation profile. For the same concentration, one may tune the effective response by tuning the concentration profile. Note that for a range of $m$ above $m = 0$ (see Fig. 4(e)), there is an increase in the SHG response with $m$ for systems with $p > 0.1$, showing that a suitable gradation profile, which amounts to suitably placing a certain fraction of the nonlinear component in the system, may provide an optimal SHG response for a given fraction of the nonlinear component. Our results show that for small total volume fraction $p$ ($p < 0.1$), a uniform profile or a profile that increases rapidly at small $z$ is beneficial, while for moderate $p$ ($p > 0.1$), there exists an optimal profile for SHG response. Note that for a given total volume fraction $p$, a gradation profile leads to nontrivial response in that the volume fraction $p(z)$ may be below the percolation threshold for some values of $z$ and above the threshold for other values of $z$. Results of our model calculations show that a gradation profile is an additional means for tuning the local field effects.

4. Discussion and conclusion

In the present work, we have investigated compositionally graded metal–dielectric composite films in which the fraction of the metallic component varies perpendicular to the film. Enhancement in the response was found for the polarization perpendicular to the film (i.e., parallel to the direction of the gradient), as a result of the continuity of the normal component of the displacement field. For the polarization parallel to the film, the physics is then governed by the continuity of the tangential component of the electric field [7]. It is also instructive to extend the present consideration to metal–dielectric composites in which the inclusion particles are graded particles, i.e., having a radial dielectric gradient. In this case, traditional theories [34] have to be modified. To this end, a differential effective dipole approximation or a first-principles approach can be used to study composites of graded particles [18]. Including nonlinear response into the consideration, it is expected that an enhanced SHG signal will result in a composite consisting of graded particles.

In summary, we have presented a formalism for evaluating the effective SHG susceptibility in com-
positionally graded metal–dielectric composite films with anisotropically shaped particles. We also carried out model numerical calculations to illustrate the effects of a gradation profile. It is found that the frequency-dependent response is highly sensitive to the degree of anisotropy of the particles. Suitably choosing the shape of the particles and the gradation profile for a given volume fraction of the particles, one may achieve tuning of an enhanced SHG susceptibility at specific frequency ranges.

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