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Optical nonlinearity enhancement via geometric anisotropy

K. P. Yuen, M. F. Law, and K. W. Yu
Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Ping Sheng
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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We investigate the effects of geometric anisotropy on the optical nonlinearity of metal nanocrystals in a dielectric host. By invoking the effective medium approximation for anisotropic composite media, we calculate the spectral density as a function of volume fraction and anisotropy. The results show that anisotropy not only changes the spectral function substantially and thereby has a pronounced effect on the nonlinearity, but also separates the absorption peak from the nonlinearity enhancement peak so that the figure of merit may be increased by orders of magnitude. We propose the use of electrorheological effect (e.g., during annealing) to realize these gains in optical nonlinearity. [S1063-651X(97)51008-7]

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I. INTRODUCTION

It is well known that optical nonlinearity of composite materials can be enhanced from those of constituent materials through the inhomogeneity of the local electric field and/or the surface-plasmon resonances [1]. Both enhancement mechanisms are sensitive to the composite microstructure.

From a previous work [2], it has been demonstrated that the optical nonlinearity can be enormously enhanced in composite wires whose cross-section area is much smaller than the length of the wires. The wire geometry means that there is a strong anisotropy in the optical response that is parallel and perpendicular to the wire. In this work, we propose the use of the electrorheological (ER) effect [3,4] to induce geometric anisotropy, e.g., during the annealing process, in material systems containing a nonlinear optical component. We consider composites made of components that are locally isotropic in their material properties, but with electric-field-induced anisotropic microstructure. It is shown that by controlling the magnitude of the applied electric field, one can vary the degree of geometric anisotropy and thereby tune the system to obtain maximum optical nonlinearity in accordance with the properties and volume fraction of nonlinear materials.

Below we use the spectral representation of the local fields [5] to model the anisotropy enhancement effect. The spectral representation is a mathematically rigorous formal expression of the effective dielectric constant ϵ_e [See Eq. (5) below]. It offers the advantage of separation of material parameters from the geometric information, which are contained in the spectral density function $m(s)$. With a given microstructure, $m(s)$ may be evaluated. With a given set of material constants, the knowledge of $m(s)$ is sufficient not only to calculate the effective dielectric constant, but also to evaluate the optical nonlinearity in the mean-field sense [6], which may be regarded as a lower bound to the accurate result. Thus, the optical nonlinearity enhancement effect is directly linked to the behavior of $m(s)$.

Consider a random metal-dielectric composite system that is initially isotropic. The spectral function is, in general, a broad continuous function that gives rise to an unimpressive nonlinear response. However, when an intense dc field is applied, e.g., during the annealing process, the ER effect can induce the formation of chainlike structures [3,4]. The spectral density is then demonstrated to contain sharp peaks, which can give rise to an enormous enhanced nonlinear response if the material system contains optical nonlinear component(s). We also show the added benefit that the frequency or volume fraction at which the enhancement peak occurs can be separated from the absorption peak, thereby further increasing the figure of merit. In what follows, we assume the particle size is much smaller than the wavelength of light so that the quasistatic approximation can be used.

II. ANISOTROPIC EFFECTIVE MEDIUM CALCULATION

In order to demonstrate the idea outlined above, we consider a composite metal-dielectric system, with metal being the nonlinear optical component. We invoke the effective-medium approximation (EMA) for anisotropic media, as proposed by Bernasconi [7]. The local constitutive relation is given by $\mathbf{D}=(\epsilon+\chi|\mathbf{E}|^2)\mathbf{E}$, where ϵ is the (position dependent) dielectric constant and χ is the (position dependent) third-order Kerr nonlinear susceptibility. We assign two different occupation probabilities parallel ($p_\parallel$) and perpendicular ($p_\perp$) to a particular direction, i.e., uniaxial anisotropy. We choose several values of the anisotropy ratio $r=p_\perp/p_\parallel$, varying from isotropic ($r=1$) to highly anisotropic ($r=0$). The coupled EMA self-consistency equations read [7]

$$p_\parallel \frac{\epsilon_1-\epsilon_\parallel}{\epsilon_1+z_\parallel\epsilon_\parallel}+(1-p_\parallel)\frac{\epsilon_2-\epsilon_\parallel}{\epsilon_2+z_\parallel\epsilon_\parallel}=0, \tag{1}$$

$$p_\perp \frac{\epsilon_1-\epsilon_\perp}{\epsilon_1+z_\perp\epsilon_\perp}+(1-p_\perp)\frac{\epsilon_2-\epsilon_\perp}{\epsilon_2+z_\perp\epsilon_\perp}=0, \tag{2}$$

where $z_\parallel$ and $z_\perp$ are the parameters parallel and perpendicular to the applied dc field, ϵ_1 and ϵ_2 are the (possibly complex) constituent dielectric functions, $\epsilon_\parallel$ and $\epsilon_\perp$ are the effective dielectric functions parallel and perpendicular to the applied dc field. In what follows, we limit ourselves to

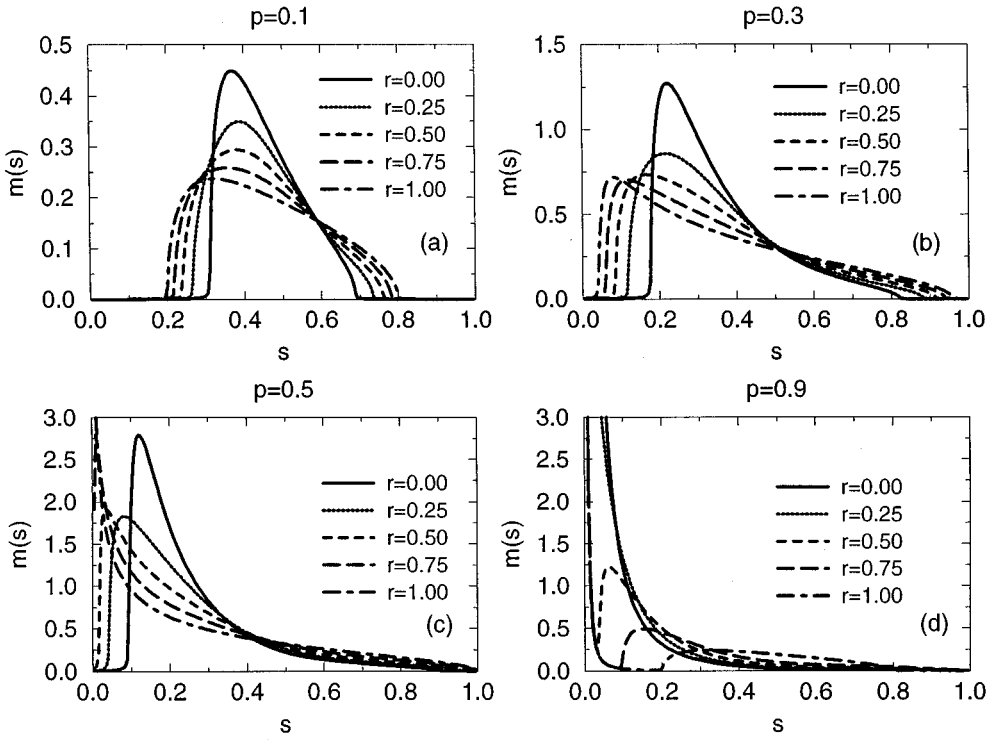

FIG. 1. Spectral density of the anisotropic EMA plotted as a function of s, for several values of $r=0$, 0.25, 0.5, 0.75, and 1. (a) $p=0.1$, (b) $p=0.3$, (c) $p=0.5$, and (d) $p=0.9$.

two dimensions (2D), where the solution is somewhat simpler. In 2D, the z parameters are given by [7]

$$z_{\|}=(\tan^{-1}\sqrt{\epsilon_{\perp}/\epsilon_{\|}})(\tan^{-1}\sqrt{\epsilon_{\|}/\epsilon_{\perp}})^{-1}, \tag{3}$$

$$z_{\perp}=(\tan^{-1}\sqrt{\epsilon_{\|}/\epsilon_{\perp}})(\tan^{-1}\sqrt{\epsilon_{\perp}/\epsilon_{\|}})^{-1}. \tag{4}$$

Since we are interested in the optical response parallel to the field direction, we can simplify our notation by letting $p=p_{\|}$ and $\epsilon_e=\epsilon_{\|}$.

For two-component composites, it has proved convenient to adopt the spectral representation of the effective linear response [5]: Let $v=1-\epsilon_1/\epsilon_2$, $w=1-\epsilon_e/\epsilon_2$, and $s=1/v$, we find

$$w(s)=\int_0^1 \frac{m(s')\mathrm{d}s'}{s-s'}, \tag{5}$$

where $m(s')$ is the spectral density which is obtained through a limiting process:

$$m(s')=\lim_{\eta\to 0^+} -\frac{1}{\pi}\mathrm{Im}w(s'+i\eta). \tag{6}$$

Equations (2)–(5) can readily be solved in the spectral representation. In our numerical calculation, we choose the realpart at several hundred equally spaced values across the interval $0\leqslant s'\leqslant 1$, and the imaginary part η to be some small positive value. The actual value of η is unimportant. We found that $\eta=0.001$ gives acceptable results by checking the sum rule,

$$\int_0^1 m(s')\mathrm{d}s'=p. \tag{7}$$

We have set $\epsilon_2=1$, and ϵ_1 is calculated from $s=s'+i\eta$.

For isotropic composites, $r=1$, $z_{\|}=z_{\perp}=1$ and the EMA self-consistency equations can be solved analytically. The spectral density is given by

$$m(s',p)=\frac{\sqrt{p(1-p)-\left(s'-\frac{1}{2}\right)^2}}{\pi s'}, \tag{8}$$

valid for $0\leqslant p(1-p)-(s'-1/2)^2$. Right at $p_c=1/2$, we have

$$m(s',p_c)=\frac{1}{\pi}\sqrt{\frac{1-s'}{s'}}, \tag{9}$$

which is indeed an exact result by virtue of the duality symmetry in 2D.

In Fig. 1, we plot the spectral density $m(s)$ against s for several values of p and r. For small p, say $p=0.1$, the metal nanoparticles form essentially isolated clusters and the spectral function exhibits a single peak centered around $s=1/2$. More interestingly, as the anisotropy increases, the spectral peak becomes narrower. This can be understood by the fact that when $r\to 0$, more chainlike isolated clusters are formed,leading to a narrow spectral peak. However, we should remark that the microstructure is still symmetric, i.e., interchanging p and $1-p$ and ϵ_1 and ϵ_2 leaves the result unchanged, even in the extreme anisotropic limit.

As p increases to 0.3, interaction among clusters occurs, leading to a broad spectral peak in the isotropic case. However, the spectral peak remains relatively narrow in the anisotropic cases. When p increases further, the metal clusters begin to percolate the system in the isotropic case, leading to a δ-function contribution to the spectral density at $s=0$. At $p=0.5$, we observe that the familiar singularity of the form of Eq. (9) occurs near $s=0$ for the isotropic case. For the anisotropic case, it is known that the percolation condition is

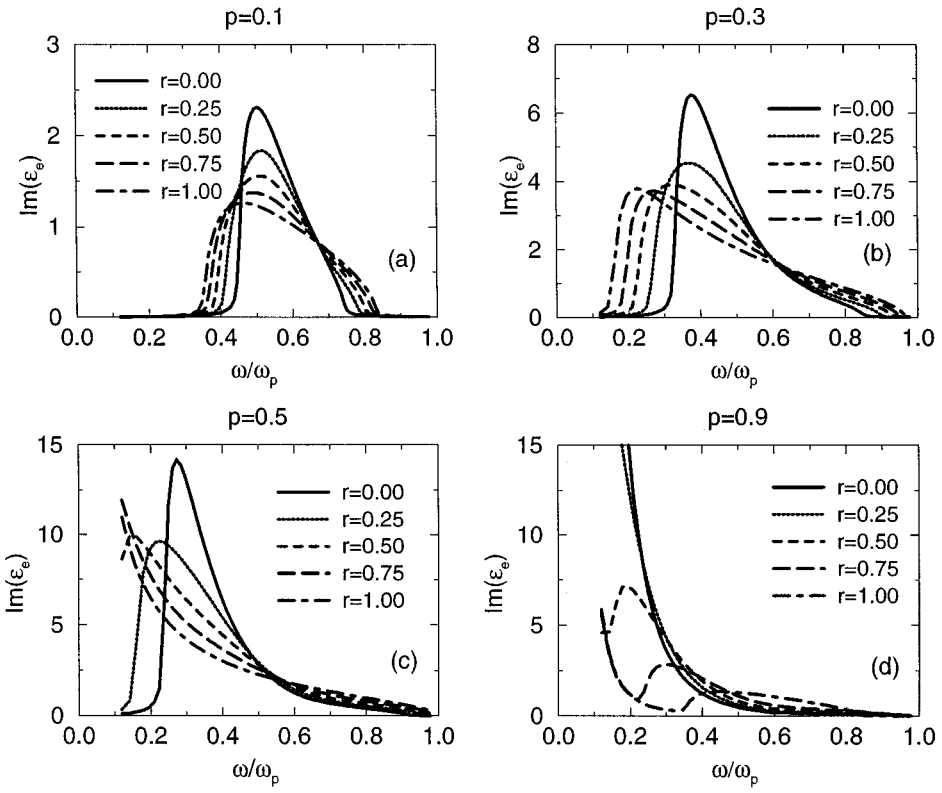

FIG. 2. The absorption peak $\mathrm{Im}(\epsilon_e)$ plotted against frequency ω, for several values of $r=0$, 0.25, 0.5, 0.75, and 1. (a) $p=0.1$, (b) $p=0.3$, (c) $p=0.5$, and (d) $p=0.9$.

$p_{\parallel}+p_{\perp}=1$. Hence, for $p=0.9$, the $r=0$ case is still below percolation. From the results, it is clear that anisotropy can change the spectral function substantially. This is the source of the pronounced effect on nonlinearity.

III. ABSORPTION AND ENHANCEMENT PEAKS IN OPTICAL RESPONSE

When the spectral density $m(s)$ is known as a function of s and p, the effective linear response can be calculated from Eq. (5). We adopt the Drude model for the dielectric function of metal nanoparticles,

$$\epsilon_1(\omega)=1-[\omega_p^2/\omega(\omega+i\gamma)], \tag{10}$$

where ω_p is the plasma frequency and γ is the damping constant. We choose $\gamma=0.01\omega_p$ and $\epsilon_2=1.77$ for our modelcalculation. In this work, we assume only the metallic component to be nonlinear.

In Fig. 2, the absorption peak $\mathrm{Im}(\epsilon_e)$ is plotted against frequency ω for various r and p. As evident from the results, the absorption peak exhibits similar behavior as the spectral density does. This is attributed to that fact that the absorption is related to the imaginary part of the effective dielectric function. From the results, it is clear that anisotropy can have an important effect on the absorption.

Other relevant physical quantities can also be calculated from the spectral representation. If a plane-polarized electromagnetic wave of amplitude E_0 with the polarization along the dc field is incident upon the suspension, the local field averages are given by [6]

$$p\langle E_1^2\rangle=\int_0^1 ds'\,\frac{s^2m(s')}{(s-s')^2}E_0^2, \tag{11}$$

$$p\langle|E_1|^2\rangle=\int_0^1 ds'\,\frac{|s|^2m(s')}{|s-s'|^2}E_0^2. \tag{12}$$

From the average local fields, we calculate the effective nonlinear response as

$$\chi_e|E_0|^2E_0^2=p\chi_1\langle|E_1|^2\rangle\langle E_1^2\rangle. \tag{13}$$

This expression results from the mean-field approximation [6]. From our calculations, we find $\langle|E_1|^2\rangle$ to be generally an order of magnitude larger than $|\langle E_1^2\rangle|$.

In Fig. 3, we plot the enhancement, $|\chi_e|/\chi_1$, against ω for various r and p. Here we observe that anisotropy has indeed a pronounced effect on the enhancement peak, as expected. As p increases, the enhancement peak exhibits a red shift, in analogy to the Maxwell-Garnett microstructure. However, the microstructure is still symmetric, although chainlike structures are formed along the dc field. We also calculated the figure of merit $|\chi_e|/\mathrm{Im}(\epsilon_e)$. For $p=0.1$, we attain the maximum figure of merit of $240\chi_1$ (esu cm) at $r=0$. We conclude that anisotropy can enhance the nonlinearity and its potential applicability.

We have also solved the EMA directly for ϵ_e and $\langle E_1^2\rangle$, without any knowledge of $m(s)$. We find that these two independent methods give identical results to within numerical accuracy.

IV. DISCUSSION AND CONCLUSION

Anisotropy is clearly a phenomenon common in most materials, and in optical phenomena. Anisotropy can be an intrinsic material property or can be induced by the application of fields. As far as optical properties are concerned, extensive investigations are found at the single crystal level. In-

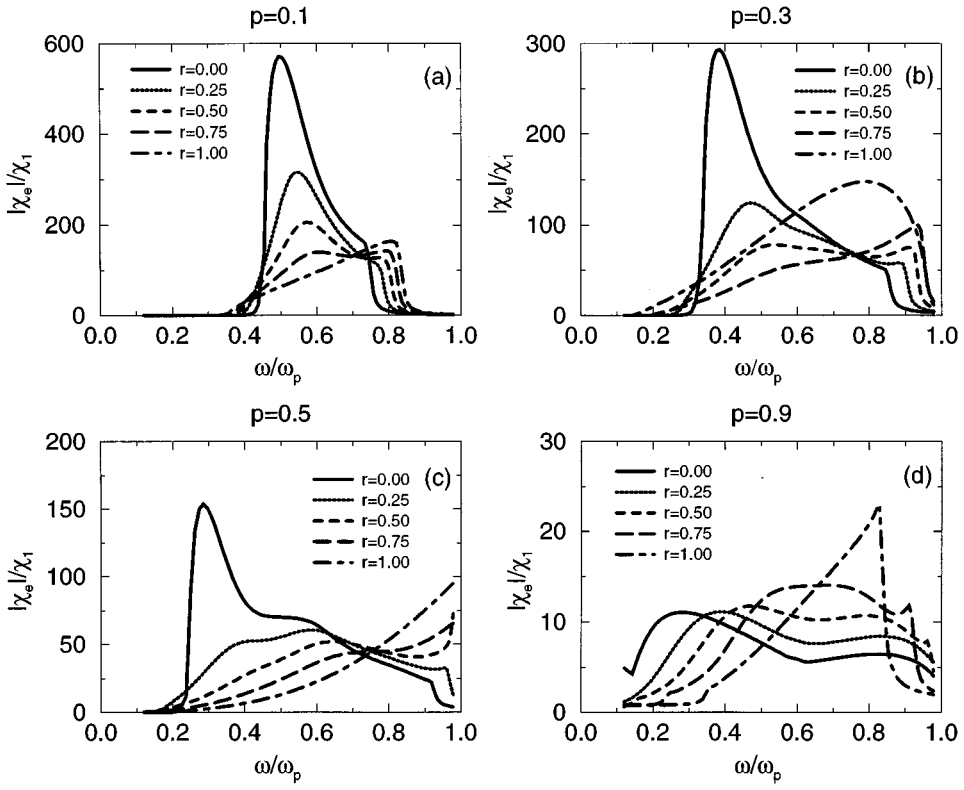

FIG. 3. The enhancement peak $|\chi_e|/\chi_1$ plotted against frequency ω, for several values of $r=0$, 0.25, 0.5, 0.75, and 1. (a) $p=0.1$, (b) $p=0.3$, (c) $p=0.5$, and (d) $p=0.9$.

duced nonlinearity such as the electrostrictive mechanism through gradients in EM fields that operates in the microsecond regime was reviewed by Neeves and Birnboim [8]. The nonlinearity can be enhanced by using nonspherical (e.g., ellipsoidal) particles [9]. A theory of enhanced Faraday rotation in composites was proposed by Hui and Stroud [10]. In this work, we consider composites made of components that are locally isotropic in their material properties, but with electric-field-induced anisotropic microstructure.

We have computed the spectral density in the anisotropic effective-medium approximation. The results support our proposal that there can be very large anisotropy-induced enhancement of nonlinearity. It is further proposed that such enhancement effect may be realized experimentally through the application of the electrorheological effect (e.g., during the annealing process), with the possibility of achieving even larger optical nonlinearity than that reported in [11]. Colloidal systems with nonlinear optical particles in the range of 0.1 μm are also good candidates for induced-anisotropy enhancement. Here the particle size range is determined by considerations that the particles should be smaller than the optical wavelength, yet large enough so that the Brownian motion is not strong enough to overwhelm the field effect (ER effect). It should be noted that when an intense dc field and an EM field are applied simultaneously, there can be an enhancement in nonlinearity due to electrostriction [8]. However, the results of the present work imply that the induced anisotropy in the microstructure can have an even more significant enhancement in nonlinearity.

In conclusion, we have investigated the effects of geometric anisotropy on the optical nonlinearity of a suspension of metal nanocrystals in a dielectric host. The results show that geometric anisotropy can change the spectral function substantially and thereby has a pronounced effect on both the nonlinearity and absorption, leading to possible large increases in the figure of merit for optical nonlinearity.

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