Magneto-controlled nonlinear optical materials

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We exploit theoretically a magneto-controlled nonlinear optical material which contains ferromagnetic nanoparticles with a nonmagnetic metallic nonlinear shell in a host fluid. Such an optical material can have anisotropic linear and nonlinear optical properties and a giant enhancement of nonlinearity, as well as an attractive figure of merit. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854719]

Finding nonlinear optical materials with large nonlinear susceptibilities and fast responses is a challenge.[1–4] Many applications of nonlinear optics that have been demonstrated under controlled laboratory conditions could become practical for technological uses if such materials were available. The most common way to obtain a nonlinear optical material is to search for materials in which the components possess an inherently large nonlinear response.[1] In contrast, in this letter we shall exploit theoretically a nonlinear optical material whose nonlinear optical properties and nonlinearity enhancement can be tuned by applying an external magnetic field—thus called *magneto-controlled nonlinear optical materials*. Devices that could benefit from these materials include optical switches, optical limiters, etc. Ferromagnetic nanoparticles, typically consisting of magnetite or cobalt, have a typical diameter of 10 nm, and carry a permanent magnetic moment.[5] As the ferromagnetic nanoparticles are suspended in a host fluid like water, they can easily form particle chains under the application of external magnetic fields,[5] thus yielding a magnetic-field-induced anisotropical structure. Recently, a nonmagnetic golden shell was used to enhance the stability of the ferromagnetic nanoparticle against air and moisture.[6]

The third-order nonlinear susceptibility χ_s of metallic (say typically, noble metals like gold and silver) shells is very large when compared to that of the magnetite or cobalt core and the host fluid like water. Let us start by considering ferromagnetic linear nanoparticles of linear dielectric constant ϵ_1'' coated with a nonmagnetic metallic nonlinear shell of ϵ_1' and χ_s which are suspended in a linear host fluid of ϵ_2. That is, in the shells, there is a nonlinear relation between the displacement $\mathbf{D}_s$ and the electric field $\mathbf{E}_s$, $\mathbf{D}_s=\epsilon_1'\mathbf{E}_s+\chi_s|\mathbf{E}_s|^2\mathbf{E}_s$, where ϵ_1' is given by the Drude form, $\epsilon_1'=1-\omega_p^2/[\omega(\omega+\gamma i)]$, where ω_p and γ stand for the plasmon frequency and the relaxation rate, respectively, and ω denotes the frequency of the incident light. In what follows, the thickness of the shell and the radius of the core are, respectively, denoted as d and R. Next, we restrict our discussion to the quasistatic approximation, under which the structured particle or the whole suspension can be regarded as an effective homogeneous one. It is known that the effective third-order nonlinear susceptibility $\overline{\chi}$ of an area is defined as[7,8]

$$\overline{\chi}=\frac{1}{V|E_0|^2E_0^2}\int_V \chi(\mathbf{r})|\nabla\phi_0(\mathbf{r})|^2[\nabla\phi_0(\mathbf{r})]^2 d\mathbf{r}, \tag{1}$$

which is in terms of zeroth-order potential $\phi_0(\mathbf{r})$ only, see Eqs. (3)–(5). In Eq. (1) E_0 denotes the external applied electric field, V the volume of the area under consideration, $\mathbf{r}$ the local position inside the medium (r the distance from the particle center to the point of interest), and $\chi(\mathbf{r})$ an $\mathbf{r}$-dependent third-order nonlinear susceptibility. To obtain the effective nonlinear susceptibility of the structured particle which contains a linear core with a nonlinear shell, we should obtain the zeroth-order potentials which are actually obtained for the system in which the nonlinear characteristic of shells disappears, $\chi_s=0$. Under the quasistatic approximation, the Maxwell equations read

$$\nabla\times\mathbf{E}=0, \quad \nabla\cdot\mathbf{D}=0, \tag{2}$$

and hence $\mathbf{E}=-\nabla\phi$, where ϕ is an electric potential. Solving Eq. (2) [or the corresponding Laplace equation $\nabla^2\phi=0$], we obtain the zeroth-order potentials for the core ϕ_0^c, the shell ϕ_0^s, and the host ϕ_0^h,

$$\phi_0^c=-c_1E_0r\cos\theta, \quad r<R, \tag{3}$$

$$\phi_0^s=-E_0(c_2r-c_3r^{-2})\cos\theta, \quad R<r<R+d, \tag{4}$$

$$\phi_0^h=-E_0(r-c_4r^{-2})\cos\theta, \quad r>R+d, \tag{5}$$

where θ is the angle between the external field and the line joining the particle center and the point under investigation, and the coefficients c_1, c_2, c_3, and c_4 are determined by the appropriate boundary conditions. Owing to Eq. (1), *the effective third-order nonlinear susceptibility of the structured particle* χ_1 can be given by

$$\chi_1\frac{\langle|\nabla\phi_0(\mathbf{r})|^2[\nabla\phi_0(\mathbf{r})]^2\rangle_{r\leqslant R+d}}{|\mathbf{E}_0|^2\mathbf{E}_0^2}=f\chi_s\frac{\langle|\nabla\phi_0(\mathbf{r})|^2[\nabla\phi_0(\mathbf{r})]^2\rangle_{R<r\leqslant R+d}}{|\mathbf{E}_0|^2\mathbf{E}_0^2}, \tag{6}$$

where f is the volume ratio of the shell to the structured particle. Thus, we obtain

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$$\chi_1 = \chi_s \frac{\beta}{\beta'}, \tag{7}$$

where $\beta=(3/5)[1/(1-f)^{1/3}-1]|z|^2z^2(5+18x^2+18|x|^2+4x^3+12x|x|^2+24|x|^2x^2)$ and

$$\beta' = \left|\frac{\epsilon_2}{\epsilon_2+(\alpha/3)(\epsilon_1-\epsilon_2)}\right|^2\left(\frac{\epsilon_2}{\epsilon_2+(\alpha/3)(\epsilon_1-\epsilon_2)}\right)^2 \tag{8}$$

with $x=(\epsilon_1''-\epsilon_1')/(\epsilon_1''+2\epsilon_1')$ and $z=(1/3)[\epsilon_2(\epsilon_1''+2\epsilon_1')]/\{\epsilon_1'[\epsilon_2+(\alpha/3)(\epsilon_1''-\epsilon_2)]\}$. In Eq. (8), the effective linear dielectric constant ϵ_1 of each structured particle can be determined by the well-known Maxwell–Garnett formula with a high degree of accuracy,

$$\frac{\epsilon_1-\epsilon_1'}{\epsilon_1+2\epsilon_1'} = (1-f)\frac{\epsilon_1''-\epsilon_1'}{\epsilon_1''+2\epsilon_1'}. \tag{9}$$

It is worth noting that for the above derivation a local field factor α has been introduced, see Eq. (8). In detail, α denotes the local field factors α_L and α_T for longitudinal and transverse field cases, respectively. Here the longitudinal (or transverse) field case corresponds to the fact that the E field of the light is parallel (or perpendicular) to the particle chain. Similar factors in electrorheological fluids were measured by using computer simulations,[9,10] and obtained theoretically[11,12] according to the Ewald–Kornfeld formulation. There is a sum rule for α_L and α_T, $\alpha_L+2\alpha_T=3$.[13] The parameter α measures the degree of anisotropy, which is induced by the applied magnetic field H. More precisely, the degree of the field-induced anisotropy is measured by how much α deviates from unity, $1<\alpha_T<3$ for transverse field cases and $0<\alpha_L<1$ for longitudinal field cases. As H increases α_T and α_L should tend to 3 and 0, respectively, which is indicative of the formation of more and more particle chains as evident in experiments.[5] So, a crude estimate of α can be obtained from the contribution of chains,[14] namely, $\alpha=[4\pi(d+R)^3/p]\Sigma_{n=1}^{\infty}n\gamma_n(H)g_n$, where p denotes the volume fraction of the structured particles in the suspension, g_n the depolarization factor for a chain with n structured particles, and $\gamma_n(H)$ the density of the chain which is a function of H. It is noteworthy that for given p $\gamma_n(H)$ also depends on the dipolar coupling constant which relates the dipole–dipole interaction energy of two contacting particles to the thermal energy. Now, the system of interest can be equivalent to the one in which all the particles with linear dielectric constant ϵ_1 [Eq. (9)] and nonlinear susceptibility χ_1 [Eq. (7)] are embedded in a host fluid with ϵ_2. For the equivalent system, it is easy to solve the corresponding Maxwell equations [Eq. (2)], in order to get the zeroth-order potentials in the particles and the host. According to Eq. (1), we obtain *the effective third-order nonlinear susceptibility of the whole suspension* χ_e as $\chi_e=p\chi_1\beta'$, which can be rewritten as

$$\chi_e = p\chi_s\beta. \tag{10}$$

The substitution of $\alpha=1.0$ (i.e., the isotropic limit) into Eq. (10) yields the same expression as derived in Ref. 8 in which the dielectric constants of the core and shell of structured particles were, however, assumed to be real rather than complex. On the other hand, the effective linear dielectric constant of the whole suspension under present consideration ϵ_e can be given by the developed Maxwell–Garnett approximation which works for suspensions with field-induced anisotropic structures[11]

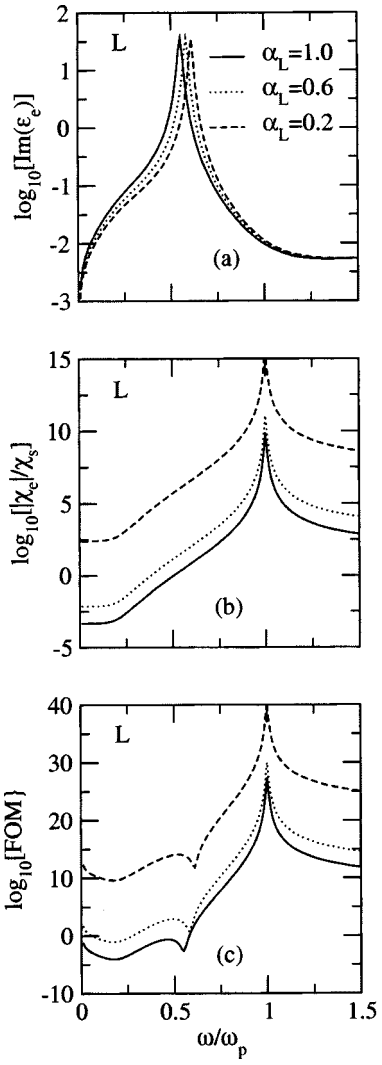

FIG. 1. (a) The linear optical absorption $\mathrm{Im}(\epsilon_e)$, (b) the enhancement of the third-order optical nonlinearity $|\chi_e|/\chi_s$, and (c) the FOM $|\chi_e|/[\chi_s\,\mathrm{Im}(\epsilon_e)]$ vs the normalized incident angular frequency ω/ω_p, for various strengths of the external magnetic field which are represented by local-field factors α_L, for longitudinal field cases (L).

$$\frac{\epsilon_e-\epsilon_2}{\alpha\epsilon_e+(3-\alpha)\epsilon_2} = p\frac{\epsilon_1-\epsilon_2}{\epsilon_1+2\epsilon_2}. \tag{11}$$

For numerical calculations, without loss of generality we take $f=0.65$, $p=0.2$, $\epsilon_1''=-25+4i$, $\epsilon_2=1.77$ (dielectric constant of water), and $\gamma=0.01\omega_p$. We further see χ_s to be a real and positive frequency-independent constant, in order to focus on the nonlinearity enhancement. Here the frequency ω is normalized by ω_p (rather than a specific value of ω_p), so that the result could be valid for general cases. The figures show that the existence of nonlinear shells causes an enhancement of nonlinearity to appear, see Fig. 1(b) and Fig. 2(b), thus yielding a large FOM, see Fig. 1(c) and Fig. 2(c). Such a nonlinearity enhancement induced by shell effects was already reported.[8] The main feature of Figs. 1 and 2 is the effects of external magnetic fields. As α_L changes from 1.0, to 0.6, and to 0.2 (namely, as α_T varies from 1.0, to 1.2, and to 1.4) the external magnetic field is adjusted from zero, to low strength, and to high strength. Due to the interaction between the ferromagnetic nanoparticles and the magnetic field, more and more particle chains are caused to appear naturally, thus yielding a magnetic-field-induced anisotropic

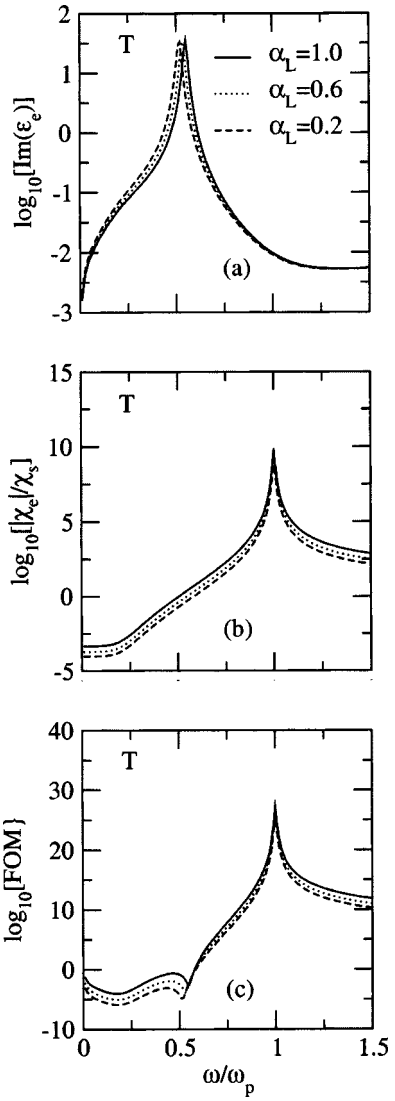

FIG. 2. Same as Fig. 1, but for transverse field cases (*T*).

structure in the suspension. It is evident to observe that the plasmon peak is caused to be blueshifted for longitudinal field cases as the magnetic field increases. However, for transverse field cases, the plasmon peak displays a redshift for the increasing magnetic field. In other words, the optical absorption is induced to be anisotropic due to the application of the external magnetic field which produces an anisotropic structure. In fact, the optical absorption arises from the surface plasmon resonance, which is obtained from the imaginary part of the effective dielectric constant. For single metallic particles in the dilute limit, it is well known that there is a large absorption when the resonant condition $\epsilon_1'+2\epsilon_2=0$ is fulfilled. When there is a larger volume fraction p of structured particles and an anisotropy α of the suspension, the effective dielectric constant should be obtained from Eq. (11), thus yielding a modified resonant condition $(1-p\alpha)\epsilon_1+(2+p\alpha)\epsilon_2=0$. So, the resonant frequency becomes larger (smaller) than the isotropic limit ($\alpha=1$) when α becomes smaller (larger) than 1. In other words, there is a blue (red) shift for the longitudinal (transversal) field cases. More interestingly, for longitudinal field cases, a giant enhancement of nonlinearity is shown as the magnetic field increases, see Fig. 1(b). In detail, the nonlinearity enhancement of a high-field case (say, $\alpha=0.2$) can be of five orders of magnitude larger than that of the zero-field case ($\alpha=1.0$). Inversely, a reduction of nonlinearity is found for transverse field cases, see Fig. 2(b). The magnitude of the nonlinearity reduction is very small in the transverse field case, when compared to that of the nonlinearity enhancement in the longitudinal field case. Owing to the giant enhancement of nonlinearity [see Fig. 1(b)], the FOM becomes much more attractive for longitudinal field cases [see Fig. 1(c)]. The FOM of a high-field case (say, $\alpha=0.2$) can even be ten-orders-of-magnitude enhanced in the longitudinal field case. However, the effect of the magnetic field on the FOM for transverse field cases seems to be uninteresting since the FOM is caused to be decreased slightly due to the nonlinearity reduction shown in Fig. 2(b). Since the permanent magnetic moment of the magnetite nanoparticles m is approximately $2.4\times10^4\ \mu_B$,[5] we can estimate the threshold magnetic field $H_c=14.3$ kA/m (or threshold magnetic induction $B_c=0.018$ T) above which the corresponding magnetic energy can overcome the thermal energy 1/40 eV so as to obtain appreciable anisotropy. Besides the magnetic energy, we should also compare the interaction energy. For instance, for two touching magnetite nanoparticles, the interaction between them is proportional to $m^2/[2(d+R)]^3$, assuming the two structured particles to be in a head-to-tail alignment. Since the magnetic moment m goes as $(2R)^3$, the interaction energy could vary as $[2R^2/(d+R)]^3$. In order to break up the two touching nanoparticles, the thermal energy should be larger than the interaction energy. So, threshold field $H_c=14.3$ kA/m serves as an upper estimate. Nevertheless, for cobalt nanoparticles, the threshold field H_c should be lower due to larger permanent magnetic moments.

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