Second-harmonic generation with magnetic-field controllabilities

C. Z. Fan and J. P. Huang[a)]
Surface Physics Laboratory (National Key Laboratory), Fudan University, Shanghai 200433, China and Department of Physcs, Fudan University, Shanghai 200433, China

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The authors theoretically exploit a class of nonlinear optical materials, which are made of single domain ferromagnetic nanoparticles coated by a nonmagnetic nanoshell with an intrinsic second-harmonic generation (SHG) susceptibility in a nonmagnetic host fluid. The SHG of such materials possess magnetic-field controllabilities, i.e., magnetic-field-controllable anisotropy, redshift, and enhancement, which are caused to appear by the shift of a resonant plasmon frequency due to the formation of the chains of the coated nanoparticles. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2356089]

Theoretical[1] and experimental[2] reports suggested that spherical particles exhibit a rather unexpected and nontrivial behavior, second-harmonic generation (SHG), due to the broken inversion symmetry at particle surfaces, despite their central symmetry which seemingly prohibits second-order nonlinear effects. In colloidal suspensions, the SHG response for centrosymmetric particles was experimentally reported.[2] Most recently, the SHG from centrosymmetrical structure has received an extensive attention (e.g., see Refs. 3 and 4). In view of recent advancements in the fabrication of nanoshells[5,6] and single domain ferromagnetic nanoparticles,[7] we shall theoretically suggest a class of nonlinear optical materials in which single domain ferromagnetic nanoparticles coated by a nonmagnetic nanoshell with an intrinsic SHG susceptibility are suspended in a nonmagnetic host fluid (Fig. 1). For such a material, there is not only an incident light, but also an external magnetic field **H**. The latter yields the formation of chains of coated nanoparticles,[8] changing the microstructure of the system and thus yielding the effective SHG with magnetic-field controllabilities. This kind of SHG is expected to receive a broad interest in the physics, optics, and engineering communities, because it is difficult or impossible to achieve with conventional, naturally occurring materials or random composites.[9–11]

When a collection of objects (e.g., coated nanoparticles or nanoparticle chains) whose size and spacing are much smaller than the wavelength λ of an incident light, the light passing through the structure cannot tell the difference, and hence the inhomogeneous structure can be seen as a homogeneous one.[12,13] In this regard, to investigate the SHG responses of the proposed material, we are allowed to average over inhomogeneous coated nanoparticles or nanoparticle chains, conceptually replacing the inhomogeneous objects by a homogeneous material (Figs. 2 and 3). Let us consider a linear ferromagnetic spherical nanoparticle with dielectric constant ϵ_1'' and radius r, which is coated by a nonlinear optical nonmagnetic nanoshell (e.g., noble metals such as silver or gold) with frequency-dependent dielectric constant $\epsilon_1'(\omega)$ and intrinsic SHG susceptibility $d_s^{ijk}(-2\omega;\omega,\omega)$ with each of the superscripts running over the three Cartesian indices. Here ω denotes the angular frequency of a monochromatic external electric field, and the radius of the whole coated nanoparticle is represented as R in the following. All the coated nanoparticles are suspended in a linear nonmagnetic host fluid of ϵ_2. In the nanoshell, the local constitutive relation between the displacement field $\mathbf{D}_s$ and the electric field $\mathbf{E}_s$ in the static case is given by $D_s^i=\Sigma_j\epsilon_1'(\omega)^{ij}E_s^j+\Sigma_{jk}d_s^{ijk}(-2\omega;\omega,\omega)E_s^jE_s^k(i=x,y,z)$, where D_s^i and E_s^i are the ith component of $\mathbf{D}_s$ and $\mathbf{E}_s$, respectively. Here $\epsilon_1'(\omega)^{ij}=\epsilon_1'(\omega)\delta_{ij}$ denotes the linear dielectric constant, which is assumed for simplicity to be isotropic. Upon certain symmetry, one can have $d_s^{iii}(-2\omega;\omega,\omega)\neq 0(i=x,y,z)$ as $d_s^{xxx}(-2\omega;\omega,\omega)=d_s^{yyy}(-2\omega;\omega,\omega)=d_s^{zzz}(-2\omega;\omega,\omega)$. 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 equivalent and effective SHG susceptibilities for the coated nanoparticle and the whole suspension, $d_1^{zzz}(-2\omega;\omega,\omega)$ [Eq. (2)] and $d_e^{zzz}(-2\omega;\omega,\omega)$ [Eq. (4)], can be extracted by considering the volume average of the displacement field at the frequency 2ω in the inhomogeneous medium. The electric field $\mathbf{E}_s$ in the nanoshell can be calculated[10] using standard electrostatics, by solving the corresponding Maxwell equation $\nabla\times\mathbf{E}_s=0$, which implies that $\mathbf{E}_s=-\nabla\phi$, where ϕ is an electric potential. Next, the equivalent linear dielectric constant $\epsilon_1(\omega)$ for the coated nanoparticle can be given by the Maxwell-Garnett formula,[9]

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

where $f=1-r^3/R^3$ is the volume ratio of the nanoshell to the whole coated nanoparticle. The solution of $\mathbf{E}_s$ in Ref. 10 can

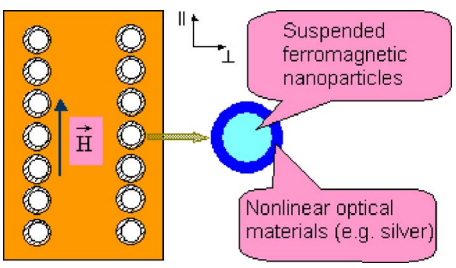

FIG. 1. (Color online) Design for a nonlinear optical material, which is subjected to an external magnetic field **H**. ∥ (or ⊥): longitudinal (or transverse) field cases corresponding to the fact that the E field of an incident light is parallel (or perpendicular) to the nanoparticle chain.

[a)]Electronic mail: jphuang@fudan.edu.cn

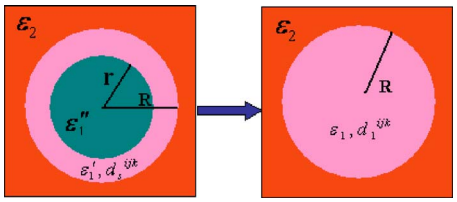

FIG. 2. (Color online) Schematic graph showing the equivalence between a coated inhomogeneous nanoparticle (left) and a homogeneous nanoparticle (right) according to Eqs. (1) and (2).

be used to derive the equivalent SHG susceptibility for the coated nanoparticle, $d_1^{iii}(-2\omega;\omega,\omega)$,

$$d_1^{iii}(-2\omega;\omega,\omega) = f d_s^{iii}(-2\omega;\omega,\omega)\sum_{j=x}^{z}\left\langle \frac{E_{s,j}(2\omega)}{E_{0,i}(2\omega)}\left(\frac{E_{s,j}(\omega)}{E_{0,i}(\omega)}\right)^2\right\rangle_s, \qquad (2)$$

where $\langle\cdots\rangle_s$ denotes a volume average over the nanoshell. To show the feature of the proposed material, we assume the optical responses [namely, $\epsilon_1(\omega)$ and $d_1^{iii}(-2\omega;\omega,\omega)$] of an equivalent spheroid or a chain (see Fig. 3) to be the same as those of each coated nanoparticle inside the spheroid or chain. For convenience, the suspension is further assumed to be the one that contains identical equivalent spheroids with geometrical depolarization factor $\alpha_\parallel$ (or $\alpha_\perp$) along the major (or minor) axis (Fig. 3). In the following, α is also called *local magnetic field factors*, because, from the physical point of view, the spheroids (or chains) are just formed due to the application of external magnetic fields. In this connection, the summation term in Eq. (2) admits $\{\Pi(2\omega)\Pi^2(\omega)+(4/5)\times(rR)^{-3}[\Pi(2\omega)p_s^2(\omega)+2\Pi(\omega)p_s(2\omega)p_s(\omega)]+(8/35)(r^3+R^3)/(r^6R^6)p_s(2\omega)p_s^2(\omega)\}/[E_{0,i}(2\omega)E_{0,i}^2(\omega)]$, where $\Pi(\omega)=T_s(\omega)E_{0,i}(\omega)$ and $p_s(\omega)=b_s(\omega)r^3T_s(\omega)E_{0,i}(\omega)$ with $b_s(\omega)=(\epsilon_1''-\epsilon_1'(\omega))/(\epsilon_1''+2\epsilon_1'(\omega))$ and $T_s(\omega)=[\Theta(\omega)+2b_s(\omega)(\Theta(\omega)-1)(1-f)]^{-1}$. Here $\Theta(\omega)=[\epsilon_1'(\omega)+2\epsilon_2]/(3\epsilon_2)$.

In the following analysis, we assume the spheroidal particle possess the same linear response as the coated particle. But, for the nonlinear response, to include the shape effect, let us introduce a local magnetic field factor α that denotes $\alpha_\parallel$ and $\alpha_\perp$ for longitudinal and transverse field cases, respectively (Figs. 1 and 3). There is a sum rule for $\alpha_\parallel$ and $\alpha_\perp$, $\alpha_\parallel+2\alpha_\perp=1$.[14] The parameter α measures the degree of structural anisotropy due to the formation of nanoparticle chains, which is induced to appear by the external magnetic field $\mathbf{H}$. More precisely, the degree of the magnetic-field-induced anisotropy is measured by how much α deviates from 1/3, $1/3<\alpha_\perp<1$, and $0<\alpha_\parallel<1/3$. As H increases, $\alpha_\perp$ and $\alpha_\parallel$ should tend to 1 and 0, respectively, which is indicative of the formation of longer nanoparticle chains (or equivalent spheroids). Therefore, α should be a function of external magnetic fields H. Specifically, for $H=0$ there is $\alpha_\parallel=\alpha_\perp=1/3$, which corresponds to an isotropic system in which all the coated nanoparticles are randomly distributed in the suspension. After the introduction of α, while we assume the spheroid possess the same nonlinear response as the coated particle, for more accurate estimation of the nonlinear response of the spheroid, let us replace $\Theta(\omega)=[\epsilon_1'(\omega)+2\epsilon_2]/(3\epsilon_2)$ with $\Theta(\omega)=[\epsilon_2+\alpha(\epsilon_1'(\omega)-\epsilon_2)]/\epsilon_2$. That is, the shape effect of spheroids has been included. Apparently, the substitution of $\alpha=1/3$ into Eq. (2) yields the same expression as the Eq. (15) in Ref. 10 in which a random composite of particles with nonlinear nonmetallic shells was investigated. Alternatively, according to the calculation of major-axis depolarization factor L of prolate spheroids,[14] $L=1/(1-\rho^2)+\rho/(\rho^2-1)^{3/2}\ln(\rho+\sqrt{\rho^2-1})$, where $\rho(>1)$ is the ratio between the major and minor axes of the elliptic cross section, α can be given in terms of the number n of nanoparticles in an equivalent spheroid (or a chain),

$$\alpha_\parallel = \frac{1}{1-n^2}+\frac{n}{(n^2-1)^{3/2}}\ln(n+\sqrt{n^2-1}). \qquad (3)$$

So far the exact relation between α and H lacks because it relates to complicated suspension hydrodynamics and kinetics at nonequilibrium. Nevertheless, the results obtained from Fig. 4 are valid for equilibrium systems in which nei-

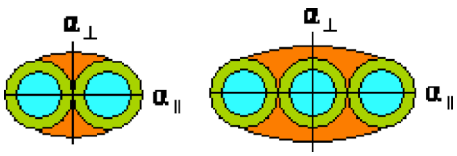

FIG. 3. (Color online) Schematic graph showing the equivalence between nanoparticle chains and spheroids with geometrical major-axis (or minor-axis) depolarization factor $\alpha_\parallel$ (or $\alpha_\perp$) [Eq. (3)]. The major axis is parallel to external magnetic fields. α is also called local magnetic field factors.

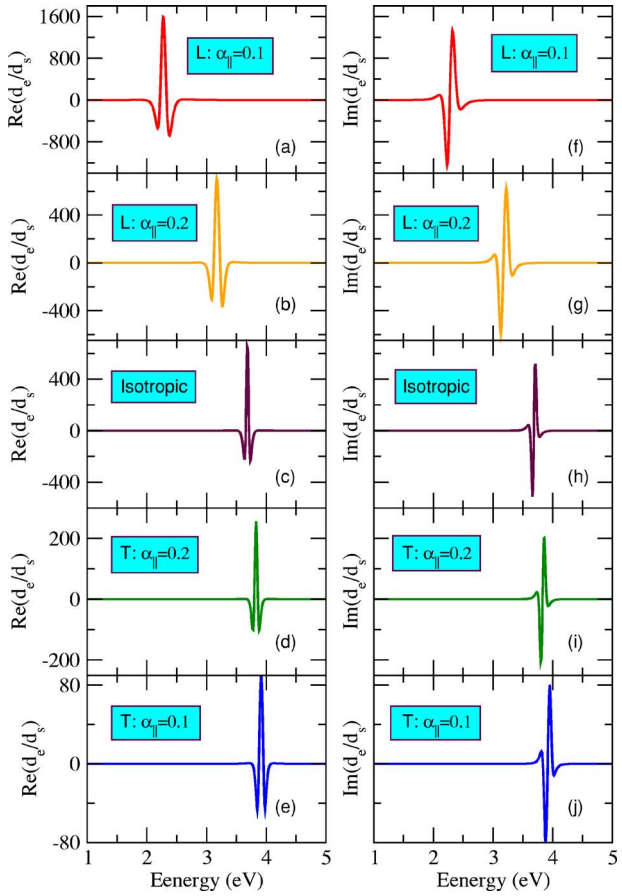

FIG. 4. (Color online) [(a)–(e)] Real and [(f)–(j)] imaginary parts of the effective SHG susceptibility $d_e^{iii}(-2\omega;\omega,\omega)\equiv d_e$ normalized by the intrinsic SHG susceptibility in the nonlinear nanoshell $d_s^{iii}(-2\omega;\omega,\omega)\equiv d_s$ for different external magnetic fields represented by local magnetic field factors $\alpha_\parallel$ vs the energy of an incident light. Here L and T denote the longitudinal and transverse field cases, respectively. According to Eq. (3), the number n of nanoparticles in the chains is $n\approx 3$ for $\alpha_\parallel=0.1$ and $n\approx 2$ for $\alpha_\parallel=0.2$. Note in (d), (e), (i), and (j) the corresponding $\alpha_\perp$ in use can be calculated according to the relation $\alpha_\parallel+2\alpha_\perp=1$.

ther hydrodynamics nor kinetics can affect the SHG. Without loss of any generality, to capture the features and their physics of the proposed materials, in Fig. 4 we use α to represent the strength of the external magnetic field H.

Now we see the suspension as the one in which the equivalent spheroids with $\epsilon_1(\omega)$ [Eq. (1)] and $d_1^{iii}(2\omega;\omega,\omega)$ [Eq. (2)] are embedded in the host fluid. Owing to the z-directed external magnetic field, all the spheroids should also be directed along z axis, but with the locations being randomly distributed. According to the general expression for the effective SHG susceptibility,[10] we take one step forward to express the effective SHG susceptibility $d_e^{iii}(-2\omega;\omega,\omega)$ for the whole suspension in the dilute limit,

$$d_e^{iii}(-2\omega;\omega,\omega) = pd_1^{iii}(-2\omega;\omega,\omega)\Gamma(2\omega)\Gamma^2(\omega), \tag{4}$$

where p is the volume fraction of the coated nanoparticles. In Eq. (4), $\Gamma(\omega)$ is a local electric field enhancement factor, and it is obtained by deriving the factor in a spheroid of depolarization factor α with principle axes along external electric fields, $\Gamma(\omega)=\epsilon_2/[\epsilon_2+\alpha(\epsilon_1(\omega)-\epsilon_2)]$.

Since metal surfaces were used to obtain enhanced SHG responses,[15] for our numerical simulations we take a Drude dielectric function (that is valid for noble metals within the frequency range of interest) for $\epsilon_1'(\omega)$, $\epsilon_1'(\omega)=\epsilon(\infty)-(\epsilon(0)-\epsilon(\infty))\omega_p^2/[\omega(\omega+i\gamma)]$, where ω_p is the bulk plasmon frequency (which is proportional to the surface plasmon frequency ω_{sp}, e.g., $\omega_p=\sqrt{3}\omega_{sp}$ for a sphere[16]), $\epsilon(\infty)$ the high-frequency limit dielectric constant, $\epsilon(0)$ the static dielectric constant, and γ the collision frequency. Specifically, for silver, $\epsilon(\infty)=5.45$, $\epsilon(0)=6.18$, and $\omega_p=1.72\times10^{16}$ rad/s.[17] In addition, we take $\gamma=0.01\omega_p$ (a typical value for metals), $r=5$ nm (a typical value for single domain ferromagnetic nanoparticles[8]), the thickness of nanoshells is 1.9 nm (or $R=6.9$ nm), $\epsilon_1''=-25+4i$ (e.g., for cobalt), frequency-independent dielectric constant $\epsilon_2=1.77$ (high-frequency limit dielectric constant of water), and $p=0.18$. Based on the values of r, R, and p, we obtain the volume fractions, p_c and p_s, of the ferromagnetic and nonlinear optical components in the whole suspension, $p_c=0.07$ and $p_s=0.11$, according to the relations $R/r=(1+p_s/p_c)^{1/3}$ and $p=p_c+p_s$. We shall investigate the light energy of 1–5 eV, which corresponds to the wavelength $\lambda=248-1242$ nm or the frequency range $\omega=1.52\times10^{15}-7.59\times10^{15}$ rad/s.

We show the effective SHG susceptibility $d_e^{iii}(-2\omega;\omega,\omega)$ of the whole suspensions in Fig. 4. For longitudinal field cases [Figs. 4(a), 4(b), 4(f), and 4(g)], as $\alpha_\parallel$ decreases (i.e., external applied magnetic field H increases and longer nanoparticle chains are formed accordingly), the resonant peak in the SHG response is not only redshifted (namely, located at a lower frequency) but also further enhanced, when compared to the isotropic case at zero external magnetic field $H=0$ [Figs. 4(c) and 4(h)]. However, inverse behavior appears for transverse field cases [Figs. 4(d), 4(e), 4(i), and 4(j)]. In detail, for transverse field cases, as the external magnetic field increases, the resonant peak in the SHG signal is both reduced and blueshifted (i.e., located at higher frequency), and hence becomes less attractive.

When the magnetic field is applied, the coated nanoparticles will form chains, thus changing the microstructure of the system accordingly. For longitudinal field cases, the nonlinear component will become more abundant along the chains than perpendicular to the chains for transverse field. When there is an incident light, the nonlinear component in the system will generally generate local potentials and fields at all harmonic frequencies. The formation of nanoparticle chains due to the application of external magnetic fields changes the surrounding circumstance of each coated nanoparticle naturally, which in turn affects the local electric field in the nanoshells and hence shifts the resonant plasmon frequency at which the resonant peak appears (Fig. 4). Therefore, in the presence of an external magnetic field, the SHG response becomes anisotropic (i.e., its strength in the longitudinal field differs from that in the transverse field), and the degree of anisotropy can further be adjusted by tuning the external magnetic field. That is, the SHG response of the system can be affected accordingly.

In looking for experimental evidence, we note that Du and Luo have reported nonlinear optical effects in suspensions of ferromagnetic nanoparticles (with mean diameter of 9 nm) in kerosene.[18] They observed that the nonlinear optical effect is enhanced by applying a moderate magnetic field. However, this mechanism was unclear at that time. Based on the present work, it seems that this enhanced nonlinear optical effect results from the induced anisotropic structure.

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