Second harmonic generation of centrosymmetric nano-spheres excited by tightly-focused doughnut beams*

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Using the vector diffraction theory and the phenomenological model, this paper investigates the second harmonic generation (SHG) of a single centrosymmetric nanosphere excited by focused doughnut beams (DBs) with different topological charges. The results show that strong backward SHG (BSHG) appears when the particle is excited by focused DBs with topological charges of ±1. The backward second harmonic radiation can be caused by the depolarized effect of high numerical aperture (NA) objectives due to the strong longitudinal components.

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Since the first observation of second harmonic generation (SHG) from centrosymmetric polystyrene microspheres by Wang et al[1], SHG of centrosymmetric particles, such as metallic particles, has attracted the special attention in scientific community[2,3]. Centrosymmetric nanoparticles can be applied in surface detection[4], chemical process monitoring, biological and chemical sensing[5] and nonlinear optical microscopy. When imaging a nanoparticle[6], backward collection mode (epi-detection) is adopted commonly, for the reason that only an objective can be utilized to focus the incident beam and collect the induced signal. However, backward second harmonic generation (BSHG) of a centrosymmetric nanoparticle is usually weak, which restricts the application of centrosymmetric nanoparticles in SHG microscopy[7]. Mertz et al[8] have found that in certain cases, strong BSHG can be provoked by adjusting the inhomogeneities in the dipole distribution. In addition, Dadap[9] has put forward that the strong BSHG can occur in the optical second harmonic (SH) scattering from cylindrical centrosymmetric particles. As a coherent nonlinear optical process, SHG actually depends on the nature of the exciting field. In our previous work, the SH response of individual centrosymmetric spherical particle illuminated by focused linearly polarized beams was examined, but backward-dominated SH radiations have not been found[7]. In this paper, doughnut beams (DBs) with different topological charges[10], which have been used to excite SHG of noncentrosymmetric nonlinear materials[11], are focused to excite SHG of a centrosymmetric nanosphere. Strong BSHG appears when the particle is excited by focused DBs with topological charges of ±1.

Fig.1 illustrates the schematic diagram of SH response from a spherical particle excited by focused DBs. As shown in Fig.1, an incoming plane wave $\boldsymbol{E}_0(\omega)$ with the fundamental frequency of ω propagates along the z axis. A spiral phase plate is used to generate doughnut beams[12]. A centrosymmetric nanosphere in the focal region is excited by the focused DBs, and the SH response is induced. The origin O of the Cartesian coordinate system and the center of the particle are both taken at the focus. α is the maximal angle determined by the numerical aperture (NA) of the objective L. $\boldsymbol{k}$ and $\boldsymbol{K}$ are the wave vectors of the fundamental incident beam and the scattered SH radiation, respectively. $\boldsymbol{r}$ and $\boldsymbol{r}_f$ are the position vectors of the particle and the detection point, respectively.

The output beam behind the spiral phase plate can be expressed as:

$$\boldsymbol{E}(\rho,\varphi,z) = \boldsymbol{x}E_0(\rho)\,\mathrm{e}^{\mathrm{i}m\varphi}\mathrm{e}^{-\mathrm{i}kz}, \tag{1}$$

where ρ and φ are the radial and polar coordinates, respectively, and m is the topological charge. According to the vector diffraction theory, the electric field in focal region can be

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obtained as[13]

$$\begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} = -A\mathrm{i}^m \begin{pmatrix} \mathrm{i}[I_m^{(+1)} + 0.5(I_{m+2}^{(-1)}\mathrm{e}^{\mathrm{i}2\varphi} + I_{m-2}^{(-1)}\mathrm{e}^{-\mathrm{i}2\varphi})] \\ 0.5(I_{m+2}^{(-1)}\mathrm{e}^{\mathrm{i}2\varphi} - I_{m-2}^{(-1)}\mathrm{e}^{-\mathrm{i}2\varphi}) \\ (I_{m+1}^{(0)}\mathrm{e}^{\mathrm{i}\varphi} - I_{m-1}^{(0)}\mathrm{e}^{-\mathrm{i}\varphi}) \end{pmatrix} \mathrm{e}^{\mathrm{i}m\varphi}, \quad (2)$$

where the integrals $I_m^{(\xi)}$ are given by

$$I_m^{(\xi)}(r,\theta) = 2\int_0^\alpha \sqrt{\cos\theta'}\sin\theta' \left(\sin\frac{\theta'}{2}\right)^{1-\xi} \left(\cos\frac{\theta'}{2}\right)^{1+\xi} \times$$
$$J_m(kr\sin\theta\sin\theta')\exp(\mathrm{i}kr\cos\theta\cos\theta')\,\mathrm{d}\theta', (\xi = -1, 0, +1). \quad (3)$$

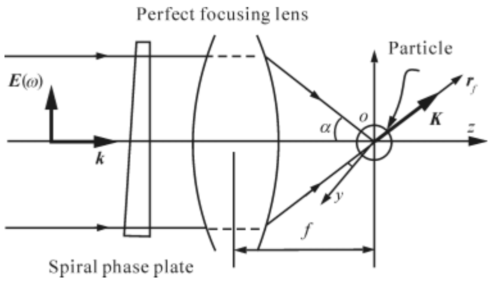

Fig.1 SHG of a single centrosymmetric nanoparticle excited by focused DBs

According to the phenomenological model, the nonlinear polarization has two nonlinear polarization sources, i.e., the local surface response and the nonlocal bulk response[14]. But when there is difference in molecular ordering between surface and bulk molecules, or when the absorbed molecules or the surface charges are used to enhance the surface response, only the SH response from the interface of the centrosymmetric nanosphere is considered, while the bulk nonlinear quadrupole response can be ignored. In fact, recent experiment has demonstrated that the surface nonlinear susceptibility is about 2 orders of magnitude larger than the bulk one[15]. At the same time, it is assumed that the nanoparticle and the surrounding medium are dispersionless, and the refractive indices of the nanosphere and the surrounding medium are taken as the same value. Under those circumstances, the Rayleigh-Gans-Debye (RGD) approximation is satisfied, which says that the existence of the nanoparticles can not disturb the distribution of the fundamental frequency field. The RGD approximation has been found to be adequate for describing nonlinear scattering from particles with diameters smaller than 200 nm[16]. In addition, we take the surface layer to be locally isotropic, which has been usually adopted in most cases of practical interest. According to the phenomenological model[14], the surface SH polarization in the local surface of a nanosphere can be expressed as

$$\boldsymbol{P}_\mathrm{s}(2\omega) = \chi_\mathrm{s} : \boldsymbol{E}(\omega)(\boldsymbol{r})\boldsymbol{E}(\omega)(\boldsymbol{r})\delta(r-a), \quad (4)$$

where $\boldsymbol{\chi}_\mathrm{s}$ is the surface second order susceptibility. In surface local coordinate system, $\boldsymbol{\chi}_\mathrm{s}$ has only three independent nonvanishing elements $\chi^{(2)}_{\mathrm{s},\perp\perp\perp}$, $\chi^{(2)}_{\mathrm{s},\perp IIII}$ and $\chi^{(2)}_{\mathrm{s},II\perp II} = \chi^{(2)}_{\mathrm{s},IIII\perp}$, where $\perp$ and *II* refer to the local spatial components perpendicular and parallel to the surface. For a spherical particle, $\boldsymbol{\chi}_\mathrm{s}$ can be written, in terms of the unit vector for the spherical coordinate system, as $\boldsymbol{\chi}_\mathrm{s} = \chi^{(2)}_{\mathrm{s},\perp\perp\perp}\boldsymbol{rrr} + \chi^{(2)}_{\mathrm{s},\perp IIII}\boldsymbol{r}(\boldsymbol{\theta\theta}+\boldsymbol{\varphi\varphi}) + \chi^{(2)}_{\mathrm{s},II\perp II}(\boldsymbol{\theta r\theta}+\boldsymbol{\varphi r\varphi}+\boldsymbol{\theta\theta r}+\boldsymbol{\varphi\varphi r})$ [14]. After translating the exciting field from the Cartesian coordinate into the spherical coordinate, the surface nonlinear polarization originating from three elements of $\boldsymbol{\chi}_\mathrm{s}$ can be expressed as:

$$\boldsymbol{P}_{\mathrm{s},\perp\perp\perp} = \chi^{(2)}_{\mathrm{s},\perp\perp\perp}(\sin\theta\cos\varphi E_x + \sin\theta\sin\varphi E_y + \cos\theta E_z)^2\boldsymbol{r},$$
$$\boldsymbol{P}_{\mathrm{s},\perp IIII} = \chi^{(2)}_{\mathrm{s},\perp IIII}[(\cos\theta\cos\varphi E_x + \cos\theta\sin\varphi E_y - \sin\theta E_z)^2 + (-\sin\varphi E_x + \cos\varphi E_y)^2]\boldsymbol{r},$$
$$\boldsymbol{P}_{\mathrm{s},II\perp II} = 2\chi^{(2)}_{\mathrm{s},II\perp II}(\sin\theta\cos\varphi E_x + \sin\theta\sin\varphi E_y + \cos\theta E_z)\times [\boldsymbol{\theta}(\cos\theta\cos\varphi E_x + \cos\theta\sin\varphi E_y - \sin\theta E_z) + \boldsymbol{\phi}(-\sin\varphi E_x + \cos\varphi E_y)] \quad . \quad (5)$$

Finally the SH polarization in the Cartesian coordinate is obtained by performing the inverse coordinate transform. The electromagnetic field at the double frequency can be obtained from $\boldsymbol{P}_\mathrm{s}(2\omega)$. In the following calculations, the excitation wavelength is 800 nm, and the diameter of the nanosphere is 100 nm. The refractive indices of the nanosphere and the surrounding medium are assumed to be 1.5 at the fundamental and double frequencies. The NA of the focusing objective is 1.4. The independent elements of $\boldsymbol{\chi}_\mathrm{s}$ take the values as $\boldsymbol{\chi}^{(2)}_{\mathrm{s},\perp\perp\perp}$ =5.02 × 10^{-18} m²/V, $\boldsymbol{\chi}^{(2)}_{\mathrm{s},\perp\parallel\parallel}$ =-2.54 × 10^{-21} m²/V and $\boldsymbol{\chi}^{(2)}_{\mathrm{s},\parallel\parallel\perp} = \boldsymbol{\chi}^{(2)}_{\mathrm{s},\parallel\perp\parallel}$ =1.13 × 10^{-20} m²/V[15,17].

Fig.2 shows the SH responses of a centrosymmetric nanoparticle excited by focused DBs with different topological charges. When m=0, which corresponds to the case of an x-polarized incident beam, the SH radiation pattern presents two lobes at an angle away from the z axis, and the forward SHG (FSHG) is prominent. However, when excited by focused DBs, the SH radiation patterns are all rotationally symmetric to the z axis. Furthermore, it is more notable that for m=±1, strong BSHG is observed in the surface SH response, and the off-axis angle is about 64°. In the backward collection mode, the focusing objective is also used to collect the signal. When NA=1.4, the maximal aperture angle α takes the value of 69°. Therefore, the backward SH signal can be effectively collected in the epi-detection.

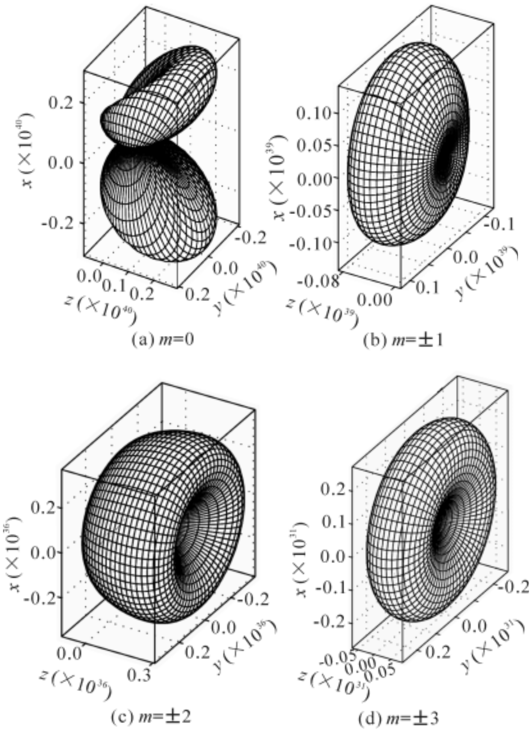

Fig.2 SH radiation patterns of a centrosymmetric nanosphere excited by focused DBs with different topological charges

In order to elucidate the backward SH response, the electric field distributions of focused DBs in the focal plane are shown in Fig.3. The circle in the center denotes the location of the particle in the focal plane. For the case of an *x*-polarized incident beam, i.e., m=0, the intensity distribution of the component E_x is rotationally symmetrical, and the maximum intensity is observed at the focus. The intensity distributions of the components E_y and E_z display symmetrical four-lobe and two-lobe, respectively. In addition, the intensities of the components E_y and E_z at the focus are both zero. In fact, the intensity distributions are closely dependent on the Bessel functions in Eq.(3). It is well known that only the zero-order Bessel function has the maximum at the origin. According to Eq.(3), when m=0, the component E_x is related to J_0, and then shows a central peak. Through examining the location of the particle in the focal plane, it can be noted that the particle radius is much smaller than the distances between the focus and the positions of the intensity maxima of the components E_y and E_z. Therefore, the effects of those components can be further ignored, and only the component E_x plays a dominant role in the surface SH response of the particle. When m=±1 or ±2, the components E_z and E_y take the maximum value at the focus, respectively. The phenomenon indicates that for different topological charges, the surface SH response is dominated by different field components, because there is difference between the SH radiation patterns when the particle is excited by focused DBs with different topological charges. The backward SHG excited by focused DBs with topological charges of ±1 is due to the strong axial components caused by the depolarized effect of high-NA objectives. With the similar mechanism, the backward SHG from self-assembled monolayers on gold by the excitation with a radially polarized beam has been observed[18].

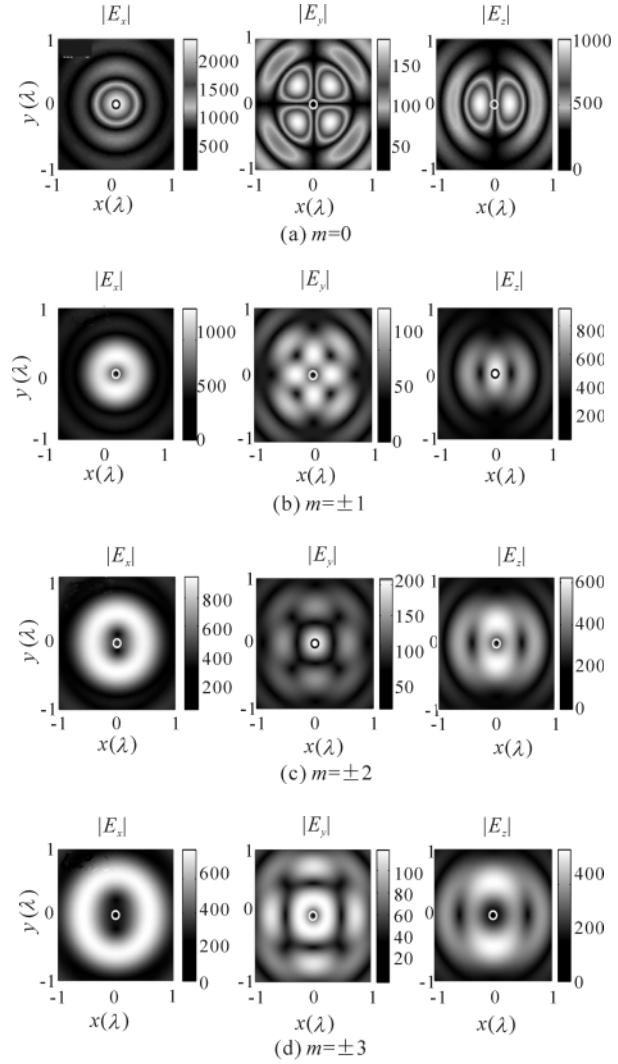

Fig.3 Intensity distributions of the three Cartesian components of the focused DBs in the focal plane with different topological charges

In summary, we investigate the SHG of a single centrosymmetric nanosphere excited by DBs with different topological charges. When m=±1, the component E_z takes the maximum value at the focus and plays a dominant role in the surface SH response of the particle, which results in strong scattering in the backward direction.

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