Second-order surface optical nonlinear response of plasmonic tip axially excited via ultrafast vector beams

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We present the second-order surface optical nonlinear response of a plasmonic tip under axial excitation of ultrafast vector beams. Theoretical calculations show that the tip has an optimized nanofocusing characteristic under axial excitation of the radial vector beam (RVB), and the electric-field intensity enhancement factor is higher than that of linear polarization beam (LPB) and azimuthal vector beam (AVB) excitations. In the experiment, the second harmonic spectra are clearly measured under three excitation beams. The intensity of the second harmonic obtained via RVB excitation is one order of magnitude higher than that of LPB and AVB excitations. © 2020 The Japan Society of Applied Physics

In recent years, second-order optical nonlinearity has attached much attention. Since there is no energy deposited onto the material during the energy conversion process, second-order optical nonlinearity has been widely explored in the fields of nonlinear frequency conversion,1–3 nondestructive label-free imaging,4) surface physical properties and dynamics,5–7) etc.

Generally, second-order optical nonlinearity is forbidden in centrosymmetric materials.6) However, the symmetry characteristic is broken at the surface of centrosymmetric materials or at the interface of two centrosymmetric materials.7–9) Thus, under excitation of the intense light, the surface/interface of the centrosymmetric materials can exhibit second-order optical nonlinearity and then radiate the second harmonic (SH).10) In addition, because the second-order surface/interface optical nonlinearity is weak,11) many approaches were adopted to compress the modal field volume to increase the electric-field intensity, thereby improving the second-order surface nonlinear conversion efficiencies. For dielectric materials, the photonic crystal and the whispering gallery cavities were used to enhance the SH radiate efficiencies due to the strong electric-field intensity of the cavity modes.12,13) The second-order surface optical nonlinearity of many plasmonic nanostructures, such as nanoparticles,14) nanorods,15) and nanodisks,16) etc, have also been reported. Based on the localized surface plasmon resonance (LSPR) effect,17,18) the strong near-field intensity can be obtained at the surface of the plasmonic nanostructures. The combination of the strong near-field intensity and the second-order surface optical nonlinearity of the plasmonic structures results in efficient second-order nonlinear optical processes.19)

The sharp metallic tip is also a typical plasmonic nanostructure.20–24) More importantly, it can be integrated with scanning probe microscopy to actively scan the analytes using the tip-enhanced nanofocusing light field. Under excitation of the continuous and ultrafast beams, the linear and third-order nonlinear optical response of the tip has been studied and further applied to super-resolution imaging.25,26) In addition, some works have also reported the second-order surface optical nonlinearity of the tip.27–29) Bouhelier et al. presented the tip-induced SH image of the focused field of the strongly converging Gaussian and Hermite–Gaussian beams.27) Labardi et al. demonstrated the polarization dependence characteristic of the tip-induced SH under excitation of the linearly polarized Gaussian beam.28)

In this letter, we present the second-order surface optical nonlinear response of the sharp metallic tip under axial excitation of the ultrafast vector beams. Theoretical simulation results show that the tip has an optimized nanofocusing characteristic under axial excitation of the focused radial vector beam (RVB), and the electric-field enhancement factor is higher than that of the linear polarization beam (LPB) and azimuthal vector beam (AVB) excitations. In the experiment, the intensity of the tip-induced SH spectrum using RVB excitation is one order of magnitude higher than that of LPB and AVB excitation, revealing that the axial excitation of RVB can effectively enhance the second-order nonlinear optical response of the sharp metallic tip.

For the tip fabricated using the noble metallic material with centrosymmetric, only the component of the second susceptibility $\chi^{(2)}_{\perp\perp}$ is selected, because it is the strongest component of the nonlinear surface susceptibility for the plasmonic tip. The surface nonlinear polarization at the SH frequency can be expressed as $P_{\perp}(2\omega, r) = \chi^{(2)}_{\perp\perp}E_{\perp}(\omega, r)E_{\perp}(\omega, r)$,30) where $\perp$ denotes the component normal to the surface of the tip apex, $E_{\perp}(\omega, r)$ is the electric-field component perpendicular to the surface of the tip apex. Note that the longitudinal electric-field components of the focused beams can be used to effectively excite the plasmonic tip to increase SH generation.

Figure 1(a) is a sketch map of the tip axially excited via the focused LPB and RVB. Gold (Au) is adopted as the material of the plasmonic tip. The cone angle of the tip is set as $\alpha = 35^\circ$, and the curvature radius of the tip apex is set as $r = 20$ nm. The 3D finite-difference time domain (FDTD) method is used to simulate the electric-field enhancement of the tip. The excitation wavelength is set as 810 nm. The permittivity of Au is obtained from Johnson and Christy,31) and the perfectly matched layers are used as the absorption boundary to simulate the structures placed in an infinitely large free space. The focused LPB calculated using the 3D-
The focused LPB and RVB, and the longitudinal electric-field component (MO) with a numerical aperture (NA) of 0.5 is used to focus the tip axially excited via LPB (d) and RVB (e). Via MO with NA focused RVB is written based on the Richards–Wolf theory, and the longitudinal electric-field components of LPB (b) and RVB (c) focused via MO with NA 0.5; Electric-field intensity distributions near the apex of the tip axially excited via LPB (d) and RVB (e).

FDTD method is adopted as the excitation source to calculate the nanofocusing of the tip. The MATLAB codes of the focused RVB written based on the Richards–Wolf theory is integrated into the 3D-FDTD software to calculate the nanofocusing of the plasmonic tip.

A long working distance (L = 15 mm) micro-objective (MO) with a numerical aperture (NA) of 0.5 is used to focus LPB and RVB, and the longitudinal electric-field component of the focused field is used to excite the tip.32) Based on the Richards–Wolf theory,33,34) the focusing characteristics of LPB and RVB are calculated with NA = 0.5. Figures 1(b) and 1(c) are the longitudinal electric-field components of the focused LPB and RVB, respectively. As shown in Fig. 1(b), the longitudinal electric-field component of the focused LPB has two lobes in the propagation direction (z-axis), and has a zero intensity in the middle. The minimum intensity will result in the absence of significant excitation of the surface plasmon resonance at the tip apex, when the tip apex is located in the center of the focal region. Nevertheless, the longitudinal electric-field component of the focused RVB not only has one lobe along the propagation direction, as shown in Fig. 1(c), but also the intensity of the longitudinal electric-field component of the focused RVB is one order of magnitude stronger than that of the focused LPB. It indicates that the significant excitation of the surface plasmon resonance at the tip apex can be achieved, when the tip is axially located at the center of the focused RVB.

Figures 1(d) and 1(e) are the calculated electric-field intensity distributions near the apex of the plasmonic tip axially excited via the focused LPB and RVB, respectively. Note that the localized surface plasmon mode can be excited at the surface of the tip under excitation of the focused LPB and RVB, but the tip has better nanofocusing properties under RVB excitation than that of LPB excitation. Under excitation of the focused LPB, the electric field is enhanced in two areas located on two sides of the tip, but not at the tip apex, as shown in Fig. 1(d). However, under excitation of the focused RVB, the electric field is not only enhanced at the tip apex, as shown in Fig. 1(e), but also the electric-field intensity enhancement factor ($EF = |E_{\text{tip}}/E_{\text{incident}}|^2$) under RVB excitation ($EF = 30$) is larger than that of LPB excitation ($EF = 8$).

The Au wire with a diameter of 250 μm is used to fabricate the tip by using the electrochemistry etching.35) Figure 2(a) is the scanning electric microscopy (SEM) image of the Au tip, the cone angle of the tip is α = 34°. The partially magnified image near the tip apex is shown in Fig. 2(b). The tip apex is hemispherical with curvature radius of $R = \sim 20$ nm, which is consistent with the structure parameters of the tip adopted in the theoretical calculation. Figure 2(c) is the scattering spectrum of the tip simulated using the 3D-FDTD method.36) Note that the tip with $R = \sim 20$ nm has LSPR effect within the wavelength range of the pump pulse (ω0), whereas there is almost no LSPR effect within the wavelength range of SH(ω0). It indicates that the electric-field of the pump pulse can be enhanced at the tip apex, while the electric-field of the SH cannot be amplified by the tip apex.

Figure 3 is the experimental setup for measuring the second-order surface optical nonlinear response of the tip, which is axially excited via LPB and RVB, respectively. The pump pulse is derived from a Ti:sapphire oscillator with central wavelength, pulse duration, and repetition frequency of 810 nm, 35 fs, and 80 MHz, respectively. The intensity of the pump pulse is adjusted via an attenuator (A). A polarizer (P) is used to purify the linear polarization of the femtosecond pulse. A half-wave plate (HWP) is used to change the polarization direction of the femtosecond pulse. When the polarization direction of the femtosecond pulse is parallel to the fast axis of the vortex plate (VP), the femtosecond pulse with Gaussian mode is converted to RVB. The transverse modal intensity distribution and the polarization examination result is shown as the inset in Fig. 3. Note that the linearly polarized beam has been converted to RVB, which has the doughnut intensity and radial polarization, simultaneously. Subsequently, a 50 × micro-objective (MO1) with NA = 0.5 and work length of 15 mm is used to focused RVB on the tip apex and collect the tip-induced SH spectrum, simultaneously. The SH spectrum is coupled into a spectrometer via MO2, after filtering the pump pulse through a dichroic mirror (DM). The tip is mounted on a displacement stage to adjust...
the position between the focus spot of the focused RVB and the tip apex. A charged coupled device (CCD) is used to observe the position of the focused spot on the tip, which is illuminated via a white light source (WLS).

The femtosecond pulse with central wavelength and average power of 810 nm and 50 mW, as shown inset in Fig. 4(a), is used to excite the tip. Figures 4(a) and 4(b) are the tip-induced SH spectra, when the tip is axially excited via LPB and RVB, respectively. Note that the SH spectra with a central wavelength of 405 nm are measured clearly, revealing that the peak power of the pump pulse and the curvature radius of the tip satisfy the SH generation. Under excitation of the focused femtosecond RVB, the tip-induced SH intensity is ∼115 counts, which is ∼8 times stronger than that of LPB excitation (∼15 counts). It indicates that the tip has a better second-order surface nonlinear optical response under RVB excitation than that of LPB excitation. Figures 4(c) and 4(d) are the calculated electric-field intensity distributions of SH near the apex of the tip excited via the focused LPB and RVB, respectively. Note that, under excitation of RVB, the electric field of SH has better local characteristics than that of LPB excitation. This means that, when the tip is axially excited via RVB, it not only improves the excitation efficiency of the SH, but also facilitates the collection of SH signal.

The second-order surface optical nonlinear response of the tip is also examined under excitation of the AVB. Under conditions of tight focusing, AVB has no longitudinal electric-field component, it only has transverse electric-field component. Figure 5(a) is the transverse modal intensity and polarization distribution of the focused AVB, under the condition of NA = 0.5. Figure 5(b) is the sketch map of the tip excited by AVB focused via a 50 × MO with NA = 0.5. The focused AVB has no longitudinal electric-field component, but if the tip apex is placed in the annular focusing region of the focused AVB, as shown inset in Fig. 5(b), the transverse electric-field component of the focused AVB is still perpendicular to the surface near the tip apex, the excitation of surface plasmon resonance near the tip apex can still be realized. Figure 5(c) is the calculated electric-field intensity distributions near the tip apex. Note that the electric-field is enhanced in two areas located on two sides of the tip, but not at the tip apex. Because the surface plasmon polaritons are excited on the two sides near the tip apex, the electric-field enhancement factor of the tip under AVB excitation is smaller than that of LPB and RVB excitations. Figure 5(d) is the tip-induced SH spectrum, when the tip is axially excited via the focused AVB. Note that the SH spectrum with central wavelength of 405 nm is clearly measured with intensity of ∼10 counts, which is smaller than that of the focused LPB (15 counts) and RVB (115 counts) excitations.

In summary, we have presented the second-order surface optical nonlinear response of the tip under excitation of the femtosecond pulse with three polarization distributions. Theoretical calculations show that the tip has the optimized nanofocusing characteristic under axial excitation of RVB, and EF is higher than that of LPB and AVB excitations. In the experiment, the intensity of the tip-induced SH spectrum...
obtained by RVB excitation is one order of magnitude higher than that of LPB and AVB excitation, revealing that the excitation of RVB can effectively enhance the second-order nonlinear optical response of the tip. The enhanced SH at the apex of the tip driven via RVB may be used as a highly confined photon source to perform high-resolution near-field optical imaging and spectroscopy.

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