Research article

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Enhanced sum frequency generation for ultrasensitive characterization of plasmonic modes

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Abstract: Highly sensitive characterization of surface plasmon resonance (SPR) modes lays the solid foundation for wide SPR-related applications. Herein, we discover that these SPR modes based on all-metal nanostructures without any probed molecule can be characterized with ultrahigh sensitivities at both excitation and emission wavelengths by utilizing plasmon-enhanced sum frequency generation (PESFG) spectroscopy. The theory of PESFG for sensitively characterizing SPR modes is first validated experimentally. Moreover, we have elaborately demonstrated that PESFG strongly depends on both the

resonant wavelengths of SPR modes and spatial mode distributions when azimuthal angles of excitations are varied. Our study not only enhances the understanding of the mechanism that governs PESFG, but also offers a potentially new method for exploring new-style SPR modes (e.g. plasmon-induced magnetic resonance and bound states in the continuum) by PESFG.

Keywords: plasmonics; surface plasmon resonance; sum frequency generation; finite-element method.

1 Introduction

Plasmonic nanostructures, based on surface plasmon resonance (SPR) [1, 2], have prompted intense interests in various areas exemplified by solar cell [3], strong coupling [4, 5], super-resolution imaging [6], and so on. Naturally, characterizing SPR modes of plasmonic nanostructures with ultrahigh sensitivities becomes critically important for understanding intrinsic mechanisms of numerous applications [7–17]. Over the past three decades, a variety of highly sensitive optical techniques, such as ultraviolet (UV)-visible infrared (IR) reflection/transmission spectroscopy [18], dark-field scattering spectroscopy [19], tip-enhanced Raman spectroscopy [6], and near-field scanning optical microscope [20], have been widely used. However, these optical techniques based on far- or near-field exhibit only linear characteristics indirectly or directly, and conventional nonlinear methods owing to complicated optical and electronic processes involved have been much less explored [21]. Therefore, beyond linear technologies, alternatives that enable nonlinear optical effects to sensitively characterize the SPR modes are highly called for.

Recently, nonlinear processes, including second-harmonic generation (SHG) [22], sum frequency generation (SFG) [23], third-harmonic generation [24], and

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four-wave mixing [25], manifest the excellent potential to sensitively characterize the SPR modes. For instance, through designing plasmon-enhanced SHG (PESHG) nanorulers, ultrahigh resolutions of approximately 1 nm have been attained with narrower linewidths than dark-field scattering spectra [22]. In addition, by generating four-wave mixing at coupled gold nanoparticles, controllable photon sources have been proposed for nonlinear near-field imaging with high resolution [25]. Particularly within the concern of the nonlinearity, SFG has attracted enormous attention due to surface/interface-sensitive capabilities [26–32]. For this SFG process, two photons at different frequencies of ω_1 and ω_2 interact and generate a new photon at the sum frequency (SF) ω_3 ($\omega_3 = \omega_1 + \omega_2$). Efforts on investigations of SFG have been devoted to (a) tailoring excitation frequencies to match vibrational frequencies of molecules and (b) tuning excitation or emission frequencies to match resonant frequencies of plasmonic nanostructures [26, 28]. Among these efforts, SPR-sensitive SFG spectroscopy has been demonstrated by (a) propagating surface plasmon polaritons (SPPs) excited in the grating and attenuated total internal reflection configurations (such as Langmuir–Blodgett layers covered on a silver film, organic films covered on silver gratings) [29, 30] or by (b) localized SPR (e.g. monolayers of octadecanethiol and dodecanethiol adsorbed on nanospheres and nanopillars, respectively) [31, 32]. These studies indicate that plasmon-enhanced SFG (PESFG) is also capable of characterizing SPR modes by introducing probed molecules to the nanostructures. In these studies, detecting and analyzing molecular information by PESFG signals with orders-of-magnitude enhancement [27, 31, 32] have been emphasized. Inevitably, introducing probed molecules leads to more complicated perturbations and stronger signal interference. Amid the immenseness of these research endeavors, the use of a PESFG-based experimental method, which provides an entrance to sensitively characterize resonance wavelength, linewidth, and resonance strength of SPR modes based on all-metal nanostructures, remains lacking in the literature.

In this work, we propose to fabricate Au nanohole arrays as the platform to explore SPR modes by PESFG. With ultrahigh sensitivities, we characterize SPR modes based on all-metal nanostructures without any probed molecule by utilizing laboratory-built PESFG spectroscopy at both the excitation and SF wavelengths under different polarizations. Validated excellently by the phase-matching equation, we also experimentally demonstrate the dependence of PESFG on resonant wavelengths of SPR modes and modes' spatial distributions.

2 Results and discussion

2.1 Design and experimental setups

In SFG, pairs of photons with frequencies ω_{IR} and ω_{VIS} generate one new photon at the SF ω_{SFG} (Figure 1A). The vibrationally excited states are populated by the IR, electronically excited states by the visible-light (VIS), and ground states with the emission of the SFG [19]. In Figure 1B, VIS and IR laser beams are overlapped temporally and spatially on the sample surface. Incident angles of both beams are 60° with respect to the surface normal, and these two beams are azimuthally spanned 5° (see Figure S1A in Supplementary Material for details). The ssp and ppp polarization configurations with conventional definition of polarization order (e.g. ssp denotes that SFG, VIS, and IR are set to s-, s-, and p-polarization, respectively) [26, 31, 32] have been used. Figure 1C shows the representative scanning electron microscope (SEM) image of the nanohole arrays, and the optical image of this sample is displayed in the inset (see Methods for a detailed fabrication procedure). We have managed to build experimental setups of SFG spectroscopy for characterizing plasmonic modes (Figure 1D) (see Methods for details). Briefly, a portion of the output from the femtosecond amplifier is used to create the tunable VIS through a second harmonic bandwidth compressor (SHBC) and a visible optical parameter amplifier (OPA) (Figure 1D). The tunable IR light is generated with IR OPA and the different frequency generation (DFG).

2.2 Validation of SFG signals

Prior to performing PESFG measurements, power- and polarization-dependent SFG measurements are carried out to confirm that the SFG signals are generated from the array surface. Generally, the SFG signal intensity can be written as follows [26, 27, 33]:

$$I(\omega_{\text{SFG}}) \propto |\chi_{\text{eff}}^{(2)}|^2 I(\omega_{\text{VIS}}) I(\omega_{\text{IR}}), \quad (1)$$

where $I(\omega_{\text{SFG}})$, $I(\omega_{\text{VIS}})$, and $I(\omega_{\text{IR}})$ denote intensities of SFG, VIS, and IR lights, and $\chi_{\text{eff}}^{(2)}$, the effective nonlinear susceptibility, respectively. For the sake of simplicity without losing the generality, the IR power is maintained as constant throughout this confirmation test and formal experiments themselves. As expected, measured SFG signal intensities vary linearly with the VIS power (Figure 2A). Usually, $\chi_{\text{eff}}^{(2)}$ can be expressed as a linear

Figure 1: Schematic diagrams and experimental setups of sum frequency generation (SFG) spectroscopy.

(A) Schematic illustration of SFG. (B) Representation of the SFG experiment. (C) scanning electron microscope image of the nanohole arrays; scale bars denote 1 μm . Inset: The optical image of the sample; scale bars for 1 cm. The color of the reflected light under white-light illumination varies with the azimuthal angles of the nanostructure due to plasmon resonances. (D) Experimental setups of sum frequency generation spectroscopy.

Figure 2: Characteristics of sum frequency generation (SFG) signals originating from the Au nanohole arrays.

(A) Power-dependent SFG signals: the SFG intensity increases with the average visible-light (VIS) powers (2–20 mW). Inset: Measured SFG intensities vs. VIS powers. (B) Polarization-dependent SFG signals: measured SFG peak values (black dots) as a function of the VIS polarization angle. The red line denotes the peak-valued fitting curve. Note that wavelengths of infrared (IR) and VIS are set to 3500 and 760 nm, and SFG and IR are fixed to p-polarizations, respectively.

combination of four possible polarization configurations as follows [33]:

$$\chi_{\text{eff}}^{(2)} = (\sin\Omega \cos\Omega_1 \cdot \chi_{\text{sps}} + \cos\Omega \sin\Omega_1 \cdot \chi_{\text{psp}}) \sin\Omega_2 + (\sin\Omega \sin\Omega_1 \cdot \chi_{\text{ssp}} + \cos\Omega \cos\Omega_1 \cdot \chi_{\text{ppp}}) \cos\Omega_2, \quad (2)$$

where Ω , Ω_1 , and Ω_2 represent polarization angles of SFG, VIS, and IR (see Figure S2 for definitions of polarization

angles). If both polarizations of SFG and IR are kept as p, we can thus simplify (2) to

$$\chi_{\text{eff}}^{(2)} = \cos\Omega_1 \cdot \chi_{\text{ppp}}, \quad (3)$$

and $I(\omega_{\text{SFG}})$ can be derived as

$$I(\omega_{\text{SFG}}) \propto |\cos\Omega_1|^2 |\chi_{\text{ppp}}|^2 I(\omega_{\text{VIS}}) I(\omega_{\text{IR}}). \quad (4)$$

As expected again, experimental SFG signal intensities behave as a cosine function does with respect to the VIS polarization angle (Figure 2B).

2.3 Agreement between reflectance spectra and PESFG signals

After confirming the SFG signals, we now demonstrate ultrahigh sensitivities of the method by PESFG. First, it is beneficial for us to choose a proper platform that features explicit SPR modes that can be excited readily. Generally, properties of the SPR modes can be characterized conveniently by the reflectance spectrum. Subsequently, we have measured reflectance spectra of the nanohole arrays at a selective azimuthal angle of 45° (see Figure S2 for the definition), without and with polarizations. We can clearly see two SPR modes (locating at ~ 633 and ~ 714 nm), which are

excited by p- and s-polarizations, respectively (Figure 3A). Correspondingly, they each possess resonance linewidths (full width at half maximum [FWHM]) down to 20 and 16 nm (Figure 3A), indicating the uniformity of our sample [18]. Therefore, we adopt the nanohole arrays accommodating clear SPR modes as an excellent platform to demonstrate the sensitivity of PESFG characterization.

Then, to consider the enhancement contribution of the excitation light to the SFG intensity, we measure the SFG signal intensity as a function of the VIS wavelength under different polarizations. For the p-polarized VIS as shown in Figure 3B, one large peak can be observed at approximately 634 nm (see Figure S3A for raw SFG spectra), when both polarizations of the IR and SFG are kept as p (i.e. ppp polarization configuration). The wavelength of IR is set to 3500 nm. In light of enhancement mechanisms in nonlinear plasmonics, the PESFG intensity can be given as [21, 34]

Figure 3: Reflectance spectra and sum frequency generation (SFG) signals at the specific azimuthal angle of 45° .

(A) Reflectance spectra under p- and s-polarization. (B, C) Visible-light (VIS) wavelength-dependent SFG intensities in ppp and ssp polarization combinations, respectively. The infrared (IR) wavelength is 3500 nm. Blue triangles indicate the resonance linewidths (full width at half maximum [FWHM]). (D) IR wavelength-dependent SFG intensities. The VIS wavelength is set to 780 nm, and polarizations of SF, VIS, and IR are set to p. Average powers of VIS and IR denote 10 and 5 mW, respectively. Note that red and blue lines represent the peak-valued fitting curve. Error bars denote the deviation of the average plasmon-enhanced sum frequency generation intensity of the arrays over multiple acquisitions on different sample areas.

$$I_{\text{PESFG}} \propto |L(\omega_{\text{IR}})|^2 |L(\omega_{\text{VIS}})|^2 |L(\omega_{\text{SFG}})|^2, \quad (5)$$

where $L(\omega_{\text{IR}})$, $L(\omega_{\text{VIS}})$, and $L(\omega_{\text{SFG}})$ denote local field enhancements of IR, VIS, and SFG lights, respectively. For example, $L(\omega_{\text{IR}}) = E_{\text{loc}}(\text{IR})/E_{\text{inc}}(\text{IR})$, in which $E_{\text{loc}}(\text{IR})$ and $E_{\text{inc}}(\text{IR})$ represent the amplitudes of the local electric field and the incident-electric field of the IR, respectively. The PESFG mechanism resembles processing methods regarding enhancements of SERS and PESHG. In SERS [35], $I_{\text{SERS}} \propto |L(\omega_p)|^2 |L(\omega_s)|^2$, and $I_{\text{PESHG}} \propto |L(\omega_p)|^4 |L(2\omega_s)|^2$ in PESHG [22], where ω_p and ω_s denote frequencies of the pump and the Stokes (or anti-Stokes) light. The PESFG, of which the enhancement behaves similarly as that of SERS and PESHG, reveals the capability of all-metal nanostructures to amplify the SFG intensity. Comparing locations of the SFG peak shown in Figure 3B and the reflectance dip in Figure 3A, we observe a satisfactory agreement (merely 1-nm deviation). Therefore, we may attribute the SFG intensity amplification to the SPR mode excited by the p-polarized VIS. This result indicates that PESFG may serve as a sensitive method for characterizing SPR modes.

Additionally, as we continue to validate the enhancement contribution of VIS with s-polarization when the polarizations of the IR and SFG are, respectively, set as p and s (i.e. ssp polarization configuration) (Figure 3C), we observe one large peak of SFG intensity at approximately 704 nm (see Figure S3B for raw SFG spectra). By contrast, the trend of SFG intensity amplification agrees with that of the reflectance spectrum under s-polarization merely qualitatively. In comparison with the spectral position of the SPR mode at ~714 nm, the peak position of the SFG intensity slightly blueshifts to ~704 nm. Although the deviation of the peak position is enlarged relative to the p-polarization situation, the deviation value of 10 nm can still show the characteristics of SPR well. This shift may stem from the newly generated weak SPR mode at 663 nm in the reflectance spectra (not marked in Figure 3A), leading to the shift of the SFG intensity enhancement toward the left (i.e. the blueshift) of 714 nm. In addition to the VIS enhancement, it is quite possible to obtain an enhancement effect when the emission (i.e. SF light) matches the SPR mode. By scanning the IR wavelength, we are capable of manipulating the SFG to move into the vicinity of the SPR mode (Figure 3D). The wavelength of VIS is set to 780 nm. As expected, we acquire one large peak at around 626 nm (see Figure S3C for raw SFG spectra), whose wavelength position exhibits a blueshift in comparison with the SPR mode at 634 nm. This discrepancy should be attributed to the deviation of the SFG emitting direction. Indeed, based on the phase-matching condition [32, 33], the SFG emission slightly deviates from the direction of 45° azimuthal angle (see Figure S1B). Consequently,

the SFG enhancement effect will be enabled toward the left (i.e. the blueshift) of 634 nm (see Figure S3D for full reflectance spectra at other azimuthal angles measured). In principle, we can also tune VIS and IR wavelengths to match the SFG with the SPR mode at 714 nm. Nevertheless, the requirement of VIS wavelength lies beyond the working scope of our experimental setups.

As shown in Figure 3, a narrow FWHM of 14 nm can be achieved from SFG spectra under the p-polarized excitation (Figure 3B), whereas the FWHM of 20 nm is observed from reflectance spectra (Figure 3A). This result indicates that SFG may have an advantage over traditional reflection spectra in terms of linewidth characterization of SPR modes. In addition, the PESFG intensity is proportional to local field enhancements of IR, VIS, and SFG lights [34], respectively. Then, we can readily obtain the information on the resonance strength from the PESFG intensity qualitatively.

In numerous practical PESFG systems, plasmonic nanostructures are generally used to amplify the SFG signals of molecules adsorbed on the surface of the nanostructure. In those PESFG systems, both nanostructures and molecules contribute to the total SFG signals [27, 31, 32]. To achieve the information on vibrational spectra and adsorption orientation of molecules, it is vital for us to quantitatively distinguish and extract the contribution from the nanostructure to total SFG signals. By sequentially characterizing the SFG of all-metal nanostructures and nanostructure-molecule systems in turn, it is possible for us to quantitatively separate the SFG signals from the molecules in the composite system. The PESFG response based on all-metal nanostructures may also lay the physical foundation for understanding the mechanism that governs PESFG jointly involved with molecules.

2.4 Dispersion relation and field distributions

To understand the mechanism that governs PESFG, we need to reveal properties of those SPR modes and their interactions and evolutions. Subsequently, measurements of reflectance spectra under different azimuthal angles are performed (Figure S3D). By extracting spectral positions of dips from reflectance spectra, we can see conspicuous modes' shifts as a function of the azimuthal angle (Figure 4A). To boost our confidence in the validity of those results, we theoretically derive the phase-matching equation [36–38], namely,

$$\frac{2\pi}{\lambda_{\text{SPP}}} \sqrt{\frac{\epsilon_{\text{Au}}}{\epsilon_{\text{Au}} + 1}} = \sqrt{\left(\frac{\sqrt{3}\pi}{\lambda_{\text{SPP}}} \sin\varphi + m \frac{2\pi}{P} \right)^2 + \left(\frac{\sqrt{3}\pi}{\lambda_{\text{SPP}}} \cos\varphi + n \frac{2\pi}{P} \right)^2}, \quad (6)$$

Figure 4: Comparisons between theoretical and experimental spectral positions of the SPP modes and corresponding electromagnetic field profiles.

(A) The spectral positions of measured $(0, -1)$ mode (black dots) and $(-1, 0)$ mode (red dots) as a function of the azimuthal angle. Theoretical curves of phase-matching equation of $(0, -1)$ mode (black line) and $(-1, 0)$ mode (red line). Triangle points denote spectral positions of simulated $(-1, 0)$ mode. (B–E) Magnetic field patterns of Hz and electric-field-vector distributions of Ex and Ey (the purple arrows) in the single nanohole cell at azimuthal angles from 15° to 45° under s polarization, respectively. Note that all intensities are normalized with the same scale bar.

where λ_{SPP} represents the SPP resonant wavelength; ϵ_{Au} , the permittivity of Au; (m, n) , the integers defining the scattering order of SPPs; φ , the azimuthal angle; and P , the period of the arrays, respectively. Based on (6), we can attribute those SPR modes to two $(0, -1)$ and $(-1, 0)$ SPP–Bloch wave modes. Moreover, monotonic trends of redshifts and blueshifts for $(0, -1)$ and $(-1, 0)$ modes with the azimuthal angle can be observed, respectively. However, we should point out that there is a plasmonic ~ 80 -nm bandgap at the 45° azimuthal angle and that it originates from the strong interference [37, 39, 40] between the $(0, -1)$ and $(-1, 0)$ modes. In addition, we note that the spectral positions of the higher energy modes between measurements and theoretical results agree with each other poorly. In the experiments, out-of-plane resonance modes can possibly be excited by components of p-polarized lights, whereas out-of-plane modes are not considered in the phase-matching equation. As a result, the remaining components of p-polarized lights are used to excite in-plane SPP modes, and hence the measurements manifest redshifts in comparison with the theoretical fitting in the high-energy region. Regardless, we will hopefully be capable of conveniently broadening resonant wavelengths of SPR modes by means of varying azimuthal angles of excitations, playing a key role in the nonlinear plasmonics [21]. Furthermore, we perform finite-element method (FEM) simulations to compute reflectance spectra of the arrays at azimuthal angles from 15° to 45° under s-polarization (see Figure S4 for details) and extract corresponding spectral positions of

dips from reflectance spectra (see triangle points in Figure 4A). Then, we study corresponding electromagnetic-field distributions (Figure 4B–E). As a result, simulated spectral positions of dips of SPR modes agree satisfactorily with those in our measurements and theories. However, the electromagnetic-field profiles manifest distinctive patterns at different azimuthal angles. Again, we expect that, by means of varying azimuthal angles of excitations, we will be capable of manipulating spatial distributions of SPR modes, whose distributions are of great importance for spatial-selectively enhancing nonlinear spectroscopy [32].

3 Conclusions

We have experimentally demonstrated ultrahigh-sensitive characterization of the SPR modes based on all-metal nanostructures without any probed molecule by PESFG. Through designing two-dimensional Au nanohole arrays as a platform, we have performed PESFG measurements with the laboratory-built reflection configuration. As a result, PESFG signals evolve closely with the reflectance spectra at both excitation and emission wavelengths, and satisfactory qualitative agreements have been obtained. Finally, we also demonstrated that the resonant wavelengths of the SPR modes and their spatial distributions exert an influence on PESFG and that these results are validated excellently by the phase-matching equation. Our

study may benefit the understanding toward the mechanism of PESFG and offer opportunities for exploring new-style SPR modes by PESFG.

4 Materials and methods

4.1 Sample preparation

The Si wafer was cleaned and dried with nitrogen gas and baked in a drying oven at 125°C for 2 h. Then, this Si substrate was spin-coated with a 200-nm layer of UV curable photoresist (Tu-170, purchased from Obducat in Sweden). After the coating, we continued to process with the nanoimprint technique. Afterward, a 2-nm chromium that served as the adhesive layer was first deposited on the substrate, and a ~100-nm gold layer was then deposited via electron-beam evaporation (FC 2000; Temescal, Santa Clara, CA, USA).

4.2 SEM characterization

After the reflectance spectra and SFG measurements, the morphology of the sample was characterized by SEM (S-4800; Hitachi, Tokyo, Japan).

4.3 SFG measurements

The SFG apparatus has been described previously [41]. In brief, a portion of the output from the femtosecond amplifier goes through an SHBC and then pumps a visible OPA to generate the tunable picosecond VIS. The rest of the output enters an IR OPA and DFG to create the tunable femtosecond IR. The VIS and IR are focused onto the surface of the sample. Then, SFG signals are collected with a spectrograph and a CCD detector after spatially and spectrally filtering. We note that parts of the polarizers are not shown in Figure 1D. Pulse widths are 150 fs and 2.5 ps, and spot sizes are 350 and 390 μm for IR and VIS, respectively. The laser repetition rate denotes 1 kHz. Energy densities of every IR and VIS pulses can be calculated as 1.3 and 2.1 mJ/cm^2 , respectively.

4.4 Reflectance calculations using FEM

We used COMSOL Multiphysics (Stockholm, Sweden) based on FEM software package to compute the reflectance spectra of the nanohole arrays with s-polarization. A three-dimensional model was built with the

periodic boundary conditions for four sides, and perfectly matched layer (PML) boundary conditions were set for the z-direction. In the z-direction, PMLs were separated with a distance of $3a$ from each side of the structure, with a thickness of a . The permittivity of Au was taken from the Drude model with $\varepsilon = 1 - \omega_p^2 / (\omega^2 + i\omega\gamma)$, $\omega_p = 1.2 \times 10^{16} \text{ s}^{-1}$, and $\gamma = 1.37 \times 10^{14} \text{ s}^{-1}$ in the simulations. A port condition was set to excite the polarized plane wave with the incident power $P_{\text{in}} = P_{\text{ia}} * S$ (P_{ia} is the time-average power density of incident fields; S is the area of one unit cell), where the s-polarized wave with components of E_x , E_y , and H_z was set. The incident and azimuthal angles (θ , φ) were thus contained into the expression of the electric fields. Then, the reflectance spectra can be calculated from $R = (P_{\text{in}} - \int_s P_{\text{av}} ds) / P_{\text{in}}$, where P_{av} is the time-average power flow over the incident plane.

Supplementary Material: See the Supplementary Material for schematic illustrations of directions; definitions of incidence, azimuthal, and polarization angles; raw SFG spectra; and the reflectance spectra.

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