

Three-dimensional electromagnetic calculations of frontal illumination TERS with a thin-film plasmonic waveguide probe

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ABSTRACT

Tip-enhanced Raman spectroscopy (TERS) is a scanning-probe-microscope-based technique for nanoscale chemical analysis. Recently, we have developed a waveguide TERS probe designed for indirectly illuminating the tops of waveguides to suppress the background signal during TERS measurements. More recently, we have shown that a front-illuminated waveguide probe substantially intensifies the incident light. However, during frontal illumination, the light enhancement principle was previously not fully understood. Therefore, we have investigated the light enhancement mechanism during the frontal illumination of a waveguide probe by three-dimensional electromagnetic calculations, revealing that the signal enhancement principles of directly and nearly directly illuminated waveguide probes are identical and that the TERS contrast is optimized when the intensity of the TERS peak of interest is maximized.

Tip-enhanced Raman spectroscopy (TERS),^{1–5} a spectroscopic technique based on scanning probe microscopy (SPM)^{6,7} and Raman spectroscopy,^{8,9} is promising for nanoscale chemical analyses on sample surfaces. TERS has been applied to a wide range of nanoscale chemical investigations, including carbon nanomaterials,^{10–13} materials for secondary batteries,^{14–16} and biomolecules.^{17–19} Beyond the diffraction limit, a high spatial resolution is achieved by locally enhancing the intensity of the incident and scattered light, mainly induced by surface plasmon resonance between the metallic probe tip and substrate. In conventional TERS, the tip and sample are directly illuminated by incident light (direct illumination).^{11,20–22} However, direct illumination TERS is usually accompanied by the degradation of the spatial resolution of TERS measurements because the radius of the incident light spot is relatively large compared to the tip radius. In contrast, indirect illumination TERS,^{18,23–28} where the sample is indirectly irradiated by the incident laser, enables this problem to be avoided.

We have recently developed an atomic force microscopy (AFM) probe coupled with an Si/Au thin-film waveguide (waveguide probe), as shown in Fig. 1(a), via focused ion beam (FIB) processing,^{28,29} and achieved indirect illumination by irradiating only the waveguide part of the probe from above, as shown in Fig. 1(b) (top illumination), suppressing the background Raman light and measuring the TERS spectrum of (4'-(pyridin-4-yl)-biphenyl-4-yl)methanethiol (4-PBT)³⁰ molecules in a stable manner. Previously, we found that the enhancement factor was higher for frontal incident (quasi-indirect) illumination of the probe than for both direct illumination of and indirect illumination from above the tip or waveguide probes, respectively,³¹ and although the large enhancement factor was supported by two-dimensional (2D) calculations,³¹ the light enhancement principle observed during quasi-indirect illumination was not fully understood, requiring three-dimensional (3D) calculations to clarify the detailed light enhancement mechanism.

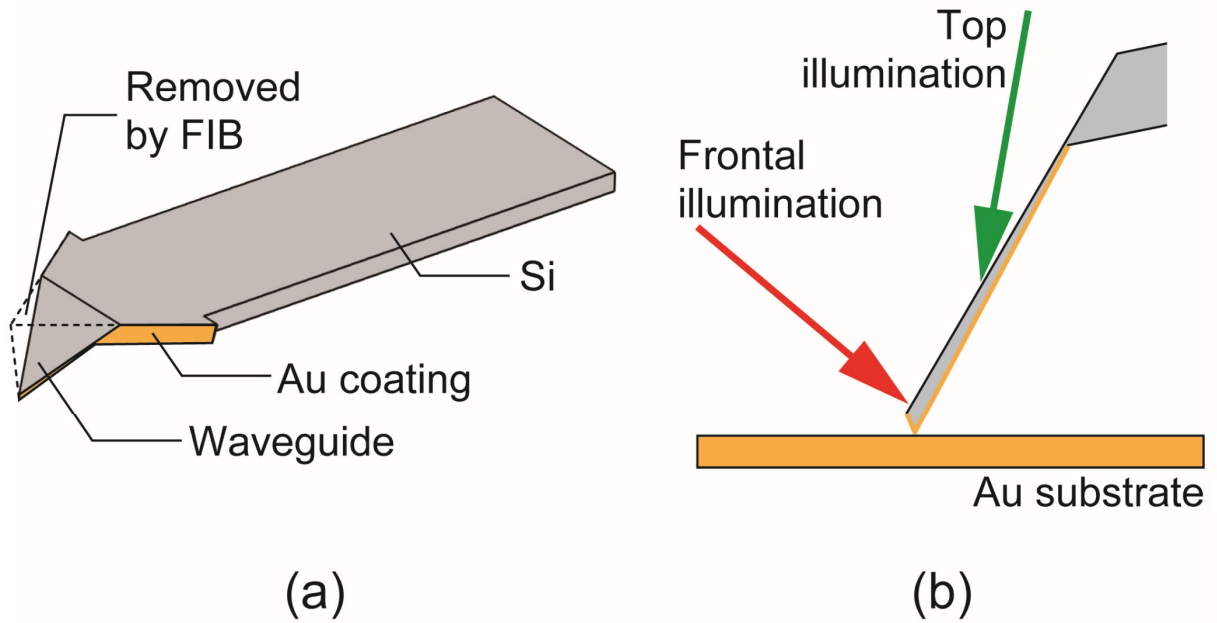


Figure 1. Schematics of the (a) TERS waveguide probe and (b) top and frontal illuminations (green and red, respectively) using the waveguide probe.

In this study, we used commercial finite element method (FEM) software (COMSOL Multiphysics®) to calculate the incident light enhancement of the waveguide probe under frontal illumination³² and clarified the light enhancement mechanism of quasi-indirect illumination by investigating the dependence of the light enhancement on the irradiation position. The results will contribute to the progress of materials research using TERS.

Other than the proposed waveguide probe, the light enhancements of several plasmonic TERS probes have been investigated by several research groups.^{33–38} For example, an Au surface/ellipsoid system was directly illuminated,³³ and a Ag nanowire probe was remotely illuminated.³⁴ Additionally, we have already used the 2D FEM model to characterize the waveguide-probe-induced light enhancement.^{24,28,31} However, to date, most calculations, including those in our previous reports, involved not 3D but 2D calculations.

Although 3D analysis should be performed for comprehending TERS principles, it is impractical because a large calculation scale requires many computational resources. Furthermore, because the indirect illumination of waveguide probes involves almost the whole waveguide, 3D calculations have not yet been achieved. However, when focusing on frontal-illumination-induced phenomena occurring only near the tip's apex region, the calculation space can be limited to the vicinity of the probe tip. Thus, the calculation scale can be reduced when considering the frontal illumination of the tip's apex. In this study, to consider effects that may have been overlooked in 2D calculations, 3D calculations were performed.

Indirect illumination suppresses background signals by avoiding direct illumination of the tip's apex (and the substrate around the tip). In contrast, we have recently shown that compared with direct illumination, frontal (quasi-indirect) illumination in the vicinity of the waveguide probe's tip can produce a very intense signal. In this study, we used 3D electromagnetic calculations to investigate the dependence of the light enhancement on the irradiation position.

Figure 2(a) shows a schematic of the 3D model for calculating the light enhancement. We assumed an Au substrate and a waveguide probe at a tip-substrate distance of 1 nm. The cantilever, which tip's radius was 50 nm, was held at 12°. The inset of Fig. 2(a) shows a magnified image of the area around the probe tip. The calculation volume is indicated by a red rectangular wireframe. The model's mirror symmetry enables computing resources to be saved. The 3D model is shown in Fig. 2(b). A *p*-polarized Gaussian incident light, which field magnitude was 1 V/m at the focal point and possessing a wavelength and a beam diameter of 660 nm and 4 μ m, respectively, was used to illuminate the tip at an incidence of 50°. Prior to the 3D calculations, we confirmed that unlike in indirect illumination from

above, in frontal illumination, the irradiation angle did not change the field enhancement factor (see Supporting Information 1). For each material, the minimum mesh size was set at one-fifth of the wavelength, a standard suggested by the software. The incident light was illuminated from the $+z$ -direction, and the positions of the incident light sources were translated along the y -axis to obtain the dependence of the light enhancement on the irradiation position. The light sources' positions were in either the mirror symmetric plane with respect to the waveguide's shape or the plane of $x = 0 \text{ } \mu\text{m}$. At each light source's position, the focal points were adjusted at the tip's surface when the light source's position ($y \geq 0 \text{ } \mu\text{m}$). The focal points were adjusted at the substrate's surface when the light source's position ($y < 0 \text{ } \mu\text{m}$). Except for the symmetric plane, the model was surrounded by perfectly matched layers (PMLs), which are not shown in Fig. 2(b), for absorbing electromagnetic waves leaving the calculation range. The symmetric plane was set as a perfect magnetic conductor (PMC), where the tangential component of the magnetic field was zero. Figure 2(c) shows the cross-sectional plane of $x = 0 \text{ } \mu\text{m}$, which is parallel to the y - z plane and includes the tip's apex. For example, this plane ($x = 0 \text{ } \mu\text{m}$) also shows a cross-sectional 2D model corresponding to the 3D model where the light source is at $y = 1 \text{ } \mu\text{m}$. Figure 2(d) shows an example of the 3D calculation results for an electric field map along the plane of $x = 0 \text{ } \mu\text{m}$ when the light source is at $y = +1 \text{ } \mu\text{m}$. Figure 2(e) shows a magnified field map at the tip-substrate gap, which describes the magnitude of the incident field enhanced by a factor of 132. To clarify the benefits of the 3D calculations, we compared the 3D calculation results to the results of the 2D calculations performed using the 2D model representing a cross-section of the corresponding 3D model (cross-sectional 2D calculation). Figure 2(f) shows the field map calculated using the 2D model extracted from the corresponding 3D model (cross-sectional 2D model). In the cross-sectional 2D calculation, the enhancement factor was underestimated, and the distributions differed for each model. Unlike the cross-sectional 2D

calculation, the 3D calculation revealed a standing wave pattern on the bottom of the waveguide, meaning that 2D calculations (including those we have performed so far) overlooked the plasmon resonance on the bottom of the waveguide. In contrast to 2D calculations, which can only characterize fields along cross-sectional planes, 3D calculations can visualize field distributions on 3D objects, such as the tip and substrate.

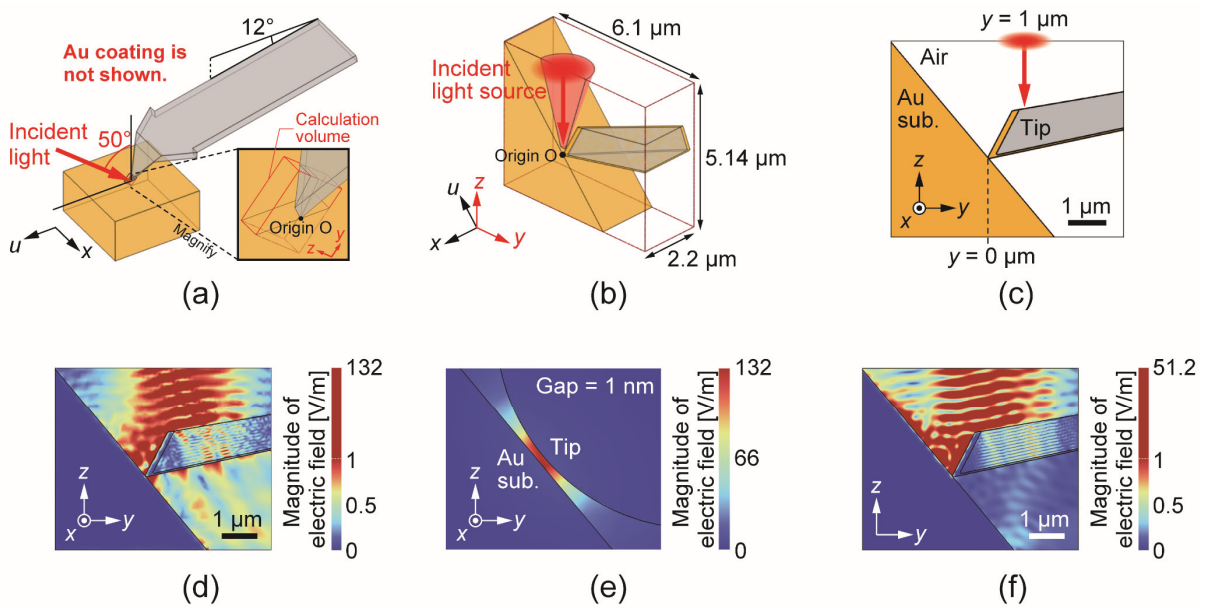


Figure 2. Schematic of the setup of the 3D electromagnetic wave simulation. The inset shows a magnified image of the area around the tip's apex. The red rectangular wireframe indicates the calculation volume. (b) A bird's eye view of the 3D calculation model. (c) A cross-sectional view of the 3D model at $x = 0 \mu\text{m}$ when the incident light source was at $y = 1 \mu\text{m}$. A cross-sectional 2D model is also shown. (d) Electric field map of the plane of $x = 0 \mu\text{m}$, calculated using the 3D model when the incident light source was at $y = 1 \mu\text{m}$. (e) Magnified electric field map shown in Fig. 2(d). (f) Electric field map computed using the cross-sectional 2D model when the incident light source was at $y = 1 \mu\text{m}$.

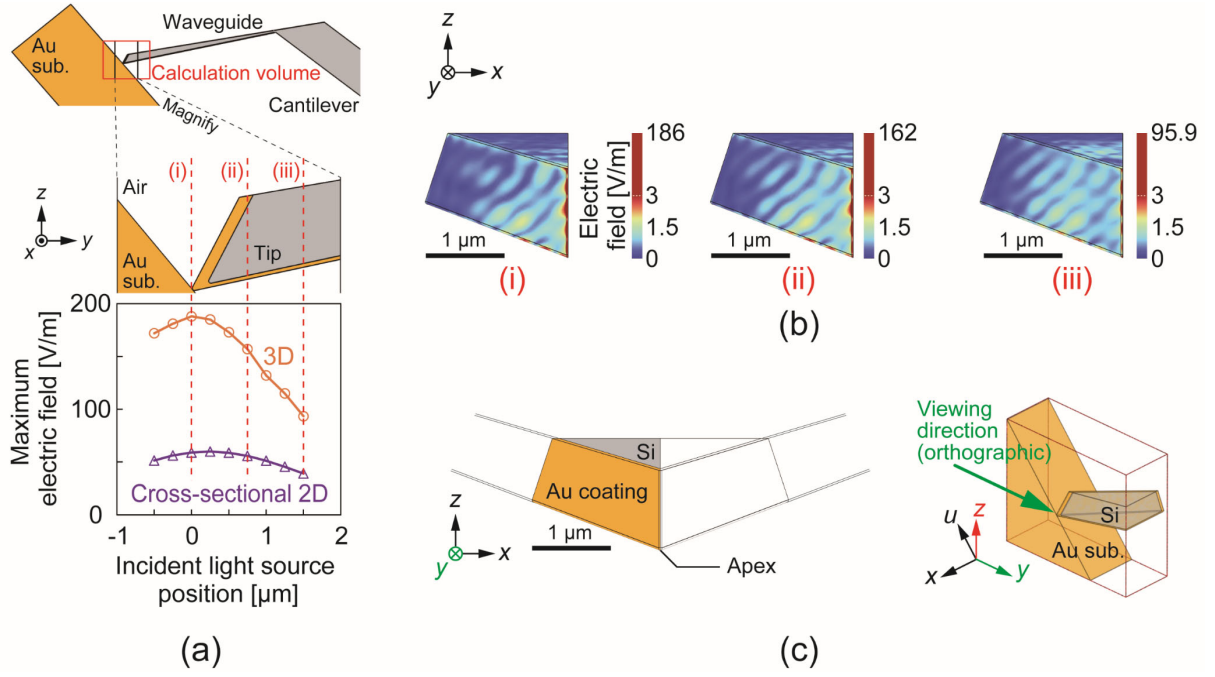


Figure 3. Results of the 3D electromagnetic wave calculations. (a) Electric field between the tip and substrate plotted as functions of the incident light source's position, as calculated using the 3D and cross-sectional 2D models. (b) Orthographic views of electric field maps on the tip's surface when the light source was at $y =$ (i) 0, (ii) 0.75, and (iii) 1.5 μm . (c) The orthographic view of the tip from the $-y$ -direction, corresponding to the field distributions shown in Fig. 3(b) (left). The viewing direction is indicated by the green arrow (right).

Figure 3(a) shows the dependence of the maximum electric field between the tip and substrate on the position of the incident light source, as calculated using the 3D and cross-sectional 2D models. The cross-sectional 2D calculations underestimated the maximum electric fields. The electric field was maximized when the light source was at $y = 0$ μm (direct illumination) and decreased as the light source moved further away from the position $y = 0$ μm (quasi-indirect illumination). Figure 3(b), which corresponds to the orthographic views of the tip from the $-y$ -direction [Fig. 3(c)], shows the field distributions on the surface of the tip when the light source was at $y = 0, 0.75,$ and 1.5 μm , as shown in Fig. 3(a). These

distributions were identical and independent of the light source's position, meaning that whether the waveguide probes were directly or quasi-indirectly illuminated, the signal enhancement principle was identical. In other words, for quasi-indirect and direct illuminations, field enhancement was based on the lightning rod and local surface plasmon resonance (LSPR) effects, respectively, as discussed in other reports^{5,39} and Supporting Information 2.

We have shown that under direct and quasi-indirect illuminations, the electric field under the tip is substantially enhanced. Next, we calculated the intensities of the Raman scattered and background lights to determine the TERS signal contrast as a function of the irradiation position of the incident light. The intensity of the Raman scattered light (I_{TERS}) is supposed to be proportional to the squared enhancement factor of the Raman scattered light multiplied by the squared enhancement factor of the incident light [Eq. (1)].^{4,40}

$$I_{\text{TERS}}(x, y, z) \propto \left(\frac{E_{\text{loc-inc}}(x, y, z)}{E_{0\text{-inc}}} \right)^2 \cdot \left(\frac{E_{\text{loc-Raman}}(x, y, z)}{E_{0\text{-Raman}}} \right)^2 \quad (1)$$

where $E_{\text{loc-inc}}$, $E_{0\text{-inc}}$, $E_{\text{loc-Raman}}$, and $E_{0\text{-Raman}}$ are the magnitudes of the electric field of the enhanced incident light, the incident light, the enhanced Raman scattered light, and the Raman scattered light, respectively. We defined the field enhancement factors of the incident light and Raman scattered light field as Eqs. (2) and (3), respectively.

$$\alpha_{\text{inc}}(x, y, z) = \frac{E_{\text{loc-inc}}(x, y, z)}{E_{0\text{-inc}}} \quad (2)$$

and

$$\alpha_{\text{Raman}}(x, y, z) = \frac{E_{\text{loc-Raman}}(x, y, z)}{E_{0\text{-Raman}}} \quad (3)$$

In conventional calculations for direct illumination TERS, α_{Raman} is usually regarded as α_{inc} (accordingly, $I_{\text{TERS}} \propto \alpha_{\text{inc}}^4$) because Raman scattered light is emitted from the position illuminated by the incident light.^{4,40,41} However, in indirect or quasi-indirect illumination

TERS, the positions illuminated by the incident light and from which the Raman light is emitted are different. Therefore, in calculations for indirect and quasi-indirect illuminations, α_{inc} and α_{Raman} should be regarded as different and, therefore, calculated separately.

Figure 4(a) shows a bird's eye view of the simulation model for α_{Raman} . We assumed that the sample molecules, which generated Raman scattered light, were uniformly aligned on the surface of the Au substrate because 4-PBT, our standard sample, formed a self-assembled monolayer on the Au surface.³⁰ The sample-generated Raman light was assumed to be a planar electromagnetic field propagating normal to the Au surface and which source was a plane on the surface of the Au substrate. The wavelength of the scattered light was assumed to be 738 nm, as determined based on the Raman shift when 4-PBT was illuminated using 660 nm incident light. The distributions of α_{inc} and α_{Raman} on the surfaces, which were 0.5 nm above the substrate surface, shown as the target region in Figure 4(a), were extracted. The extracted surface was a $2 \times 2 \mu\text{m}$ square region centered just under the tip's apex. Figures 4(b) and 4(c) shows the distributions of α_{inc} and α_{Raman} , respectively, when the light source was at $y = 1 \mu\text{m}$. Notably, a bright blue area appeared from the center to the lower right corner of the distribution of α_{inc} in Fig. 4(b). This contrast was attributed to the laser light reflected by the side of the Au-coated waveguide. The concentrated electric field on the edge between the side and bottom also affected this contrast, which is why the bright blue area was outside the triangular-shaped shade cast by the waveguide. By multiplying the second powers of the distributions of α_{inc} and α_{Raman} , the I_{TERS} distribution was derived, as shown in Fig. 4(d). The values obtained by multiplying the second powers of α_{inc} and α_{Raman} were not exactly I_{TERS} but values proportional to I_{TERS} . However, for simplicity, we treated the obtained values as I_{TERS} because for actual TERS experiments, absolute values are not of interest. Then, we defined the TERS and background signals (S_{TERS} and S_{BG}) as integrals of I_{TERS} on the half-circular region within a radius of 20 nm from the position just under the tip's apex and on the

remaining region included in the extracted range (except for the region concerning S_{TERS}), respectively. Consequently, the total spectrometrically detected signal (P_{total}) was expressed as Eq. (4).

$$P_{\text{total}} = S_{\text{TERS}} + S_{\text{BG}}, \quad (4)$$

and the TERS signal contrast (C_{TERS}) was defined as Eq. (5).

$$C_{\text{TERS}} = S_{\text{TERS}}/S_{\text{BG}}. \quad (5)$$

Higher C_{TERS} values mean that TERS imaging was less influenced by the background scattered light.

Figure 4(e) shows the calculated dependences of P_{total} and C_{TERS} plotted as functions of the position of the incident light source's position. When the light source was at $y = 0.25 \mu\text{m}$, C_{TERS} was maximized. Thus, the effect of the background Raman scattered light was suppressed better when the Au-coated edge behind the tip's apex was illuminated than when the tip's apex itself was illuminated. However, at approximately the peak C_{TERS} , the dependence of C_{TERS} on the light source's position was quite low. Therefore, the adjustment of the incident focal point to the position producing the most intense signal (P_{total}) for a spectrometer is also reasonable in experiments for establishing practical applicability.

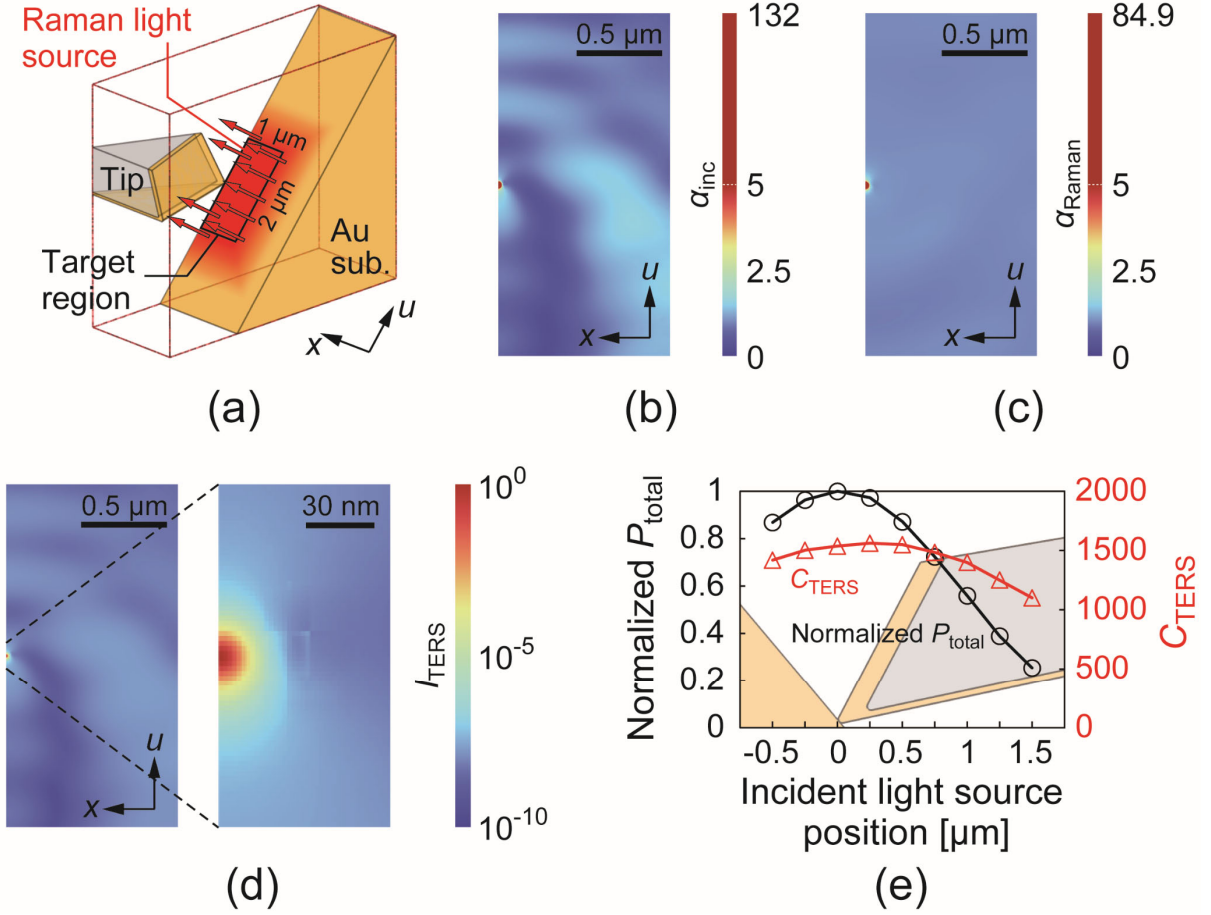


Figure 4. (a) A bird's eye view of the 3D simulation model for α_{Raman} . (b) The α_{inc} distribution when the incident light source was at $y = 1 \mu\text{m}$. (c) The α_{Raman} distribution. (d) The I_{TERS} distributions derived from Figs. 4(b) and 4(c). (e) The calculated dependences of the spectroscopy-detected total signal (P_{total}) and TERS contrast (C_{TERS}) on the position of the incident light source. To clarify the relation to the geometry, the plots are overlapped with the schematic of the waveguide model.

These calculations imply that for the frontal illumination method, only the front edge of the waveguide (rather than the whole waveguide) must be used. Thus, the waveguide does not have to be formed over the whole tip. For maximizing C_{TERS} , processing at approximately 3 μm from the apex is sufficient. Then, we designed probes which tip ends possessed a short

waveguide (shortened-waveguide probes), as described in Supporting Information 3, and used the shortened-waveguide probes to obtain TERS spectra, as described in Supporting Information 4. Notably, when used with the quasi-indirect method, the waveguide and shortened-waveguide probes possessed the same performance. The experimental results, including the TERS performance and spatial resolution, are detailed in our previous paper.³¹ In all the experiments, C_{TERS} and the spatial resolution were several thousands and 22 nm, respectively.

As the shortened-waveguide probe was fabricated using an Si thin film asymmetrically coated with Au, incident laser-induced thermal bending of the thin film may have affected the mechanical stability of the probe. Therefore, we conducted a thermomechanical FEM simulation to determine the probe's stability, as detailed in Supporting Information 5. The probe's shortened-waveguide part bent approximately 15 pm, indicating that the probe possessed good thermal stability.

Finally, we compared the field enhancement of the quasi-indirect illumination with those of other combinations of probes and illumination methods. Thorough 2D calculations, we have already shown that the frontal illumination of the waveguide probe generated a more intense Raman signal than both the illumination of the waveguide probe from above and the frontal illumination of an Au-coated cantilever probe (OMCL-AC240TS, Olympus).³¹ Additionally, we used 2D calculations to evaluate the field enhancements of waveguide and unprocessed probes (an Au-coated ArrowTM NC probe, Nanosensors) (see Supporting Information 6). Without FIB milling, the front Au coating reflected the incident light, and the reflected light did not contribute to the light enhancement. In contrast, with FIB milling, the front Au coating was removed, and the exposed Si transmitted the incident light to the

bottom-side Au film, increasing the enhancement factor. Therefore, FIB milling played an important role in Raman signal enhancement.

In conclusion, the light enhancement characteristics of a front-irradiated waveguide probe were calculated using 3D electromagnetic wave FEM models. The 3D calculations revealed that the 2D calculations underestimated the enhancement factors and that an SPP-induced standing wave pattern occurred on the Au surface. When the irradiation position was within several micrometers of the tip's apex, the light enhancement principles of the lightning rod effect and LSPR were common, regardless of the irradiation position. In addition, the enhancement factors of the incident and Raman fields were separately computed. The spectroscopically detected Raman signal was maximized when the tip's apex was directly illuminated, and the influence of the background light slightly decreased when the Au-coated edge behind the tip's apex was illuminated. Under both conditions, because the background influence was almost identical, the former condition was suggested for simply operating the TERS system. Lastly, TERS was measured using a front-illuminated shortened-waveguide probe. We obtained TERS signals for 4-PBT molecules by comparing the spectra generated with and without using a tip-sample contact. These results strongly support the practical applicability of TERS measurements conducted using front-illuminated waveguide probes. As the demonstrated TERS probe was compatible with conventional AFM-TERS systems, it should be used in many research fields and contribute to the advancement of the characterization and development of various materials.

ASSOCIATED CONTENT

Supporting Information.

Angle dependence of the electric field enhancement in frontal and top illuminations using the waveguide probe (SI1); lightning rod effect and local surface plasmon resonance (LSPR) effect (SI2); fabrication of a shortened-waveguide probe (SI3); TERS spectrum acquired using a shortened-waveguide probe (SI4); thermomechanical simulation of the stability of an Si waveguide asymmetrically coated with Au and exposed by the incident laser (SI5); comparison of the electric field enhancement between the waveguide probe and an unprocessed probe (SI6). (PDF)

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Author Contributions

The simulation was designed, performed and summarized by M. I. with feedback from K. Z. and K. K. The probes were designed and fabricated by L. L. with the assistance of K. Z. and K. K. The measurements were performed by M. I. with the assistance of K. K. The study was supervised by K. K. The manuscript was written by M. I. and K. K. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

TERS, tip-enhanced Raman spectroscopy; SPM, scanning probe microscopy; AFM, atomic force microscopy; FIB, focused ion beam; 4-PBT, (4'-(pyridin-4-yl)-biphenyl-4-yl)methanethiol; 2D, two-dimensional; 3D, three-dimensional; FEM, finite element method; PML, perfectly matched layer; PMC, perfectly magnetic conductor; LSPR, local surface plasmon resonance; SEM, scanning electron microscopy; SPP, surface plasmon polariton.

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TOC Graphic

