Hindawi
Journal of Nanotechnology
Volume 2018, Article ID 3898524, 6 pages
https://doi.org/10.1155/2018/3898524

Research Article

Simple Modeling of the Ratio of Fields at a Tip and a Contacting Surface with External Illumination

E. Bortchagovsky

Institute of Semiconductor Physics of NAS of Ukraine, Pr.Nauki 41, Kyiv 03028, Ukraine

Correspondence should be addressed to E. Bortchagovsky; bortch@yahoo.com

Received 5 May 2018; Accepted 14 June 2018; Published 1 August 2018

Academic Editor: Paresh Chandra Ray

The analysis of the relation of fields generated at a tip and a contacting surface is performed in the Rayleigh approximation of a simple dipole model for the standard configuration of tip-enhanced Raman scattering experiments with external excitation. A comparison of the present results with the previous ones obtained for the case of tip-source reveals the role of tip-surface configuration as the amplifier of the exciting field and the stronger influence of roughness on the field distribution at external illumination, as roughness is directly excited by the external field producing second source of field in addition to the tip.

1. Introduction

A previous study [1] considered the ratio of fields at a tip and a contacting surface calculated in the dipole approximation in static limit (Rayleigh approximation) for the case of tip-source. The analysis revealed the influence of surface plasmons on the metallic surface, which makes the field at the plane surface slightly higher than the field at the tip with small tip-surface separation. It happens in spite of the fact, that it is the tip, which is the primary and the only source of the field in the considered system.

However, in spite of the fact that the use of a tip-source is favorable for tip-enhanced Raman scattering (TERS) [2], until now tetrahedral tip demonstrating excellent properties in TERS [2, 3] is the only literal tip-source without external illumination, which has simple construction. Another proposed construction [4] is much more complex in the preparation and practically exaggerates the list of tip-sources. One more possible variant [5, 6] was not yet used for TERS. Until now, the main TERS configuration is the external illumination of the tip apex by a focused light beam.

Thus, this article is devoted to the analysis of the standard case of the TERS configuration with external illumination. The aim is to reveal the angular dependency of fields and the change of the external field at different distances to the surface due to interference of incident and reflected light. As well as, in the previous article [1], the main attention is devoted to the behavior of the ratio of fields at the tip apex E_t and at the surface E_s, calculated on the basis of the same simple dipole model. As it was noticed previously [1], the used simple approach is not appropriate for modeling the whole field distribution and determining the absolute field values but is rather robust just to analysis of the ratio of fields. The latter is enough to compare enhancement conditions at the tip apex and at the contacting surface, which is necessary for the application of functionalized tips as Raman probe [7] and their use as an internal standard in TERS [8].

2. Plane Surface

In contrast to the case of tip-source, which is the primary source of the field, external illumination excites the tip and contributes to the field at any point of the system. As in the previous study, the tip is modeled as a spherical particle, the polarizability of which in Rayleigh approximation is given by a standard expression [9]:

$$\alpha_t = R_t^3 \frac{\varepsilon_t - \varepsilon_a}{\varepsilon_t + 2\varepsilon_a}, \quad (1)$$

which includes the radius of the particle R and dielectric functions of the tip material ε_t and the ambient ε_a. In such an approach, the sphere is substituted by the dipole situated at the center of the sphere with given isotropic polarizability. It is well known that approaching a surface renormalizes polarizability of a dipole due to its interaction with its own image in the surface [9] to

$$\alpha_i^* = \frac{\alpha}{1 - \nu_i \alpha K / 8z^3}, \quad (2)$$

what generates anisotropy with $\nu_i = 1$ for the longitudinal polarizability along the surface and $\nu_i = 2$ for the transverse polarizability perpendicular to the surface. z is the distance from the center of the sphere to the surface, and K is the static reflection coefficient:

$$K = \frac{\varepsilon_a - \varepsilon_s}{\varepsilon_a + \varepsilon_s}, \quad (3)$$

where ε_a is the dielectric function of the ambient and ε_s the dielectric function of the surface. It was underlined in [1] that this coefficient is bigger than the unit for metallic surfaces supporting surface plasmons, which makes the dipole image larger than the source one and creates the minimum close to the surface in the distance dependency of the ratio of fields at the tip apex and at the surface.

With the external illumination, the field exciting the tip is the sum of fields of the incident light and light reflected by the surface. Besides the angle of incidence φ and Fresnel reflection coefficients r_p and r_s for p- or s-polarization, respectively, this field is also defined by the distance to the surface z. If to define the phase of the field on the surface as zero, the fields are:

$$\begin{aligned} E_x &= E_p\left(e^{-ikz\cos\varphi} - r_p e^{ikz\cos\varphi}\right)\cos\varphi, \\ E_y &= E_s\left(e^{-ikz\cos\varphi} + r_s e^{ikz\cos\varphi}\right), \\ E_z &= E_p\left(e^{-ikz\cos\varphi} + r_p e^{ikz\cos\varphi}\right)\sin\varphi, \end{aligned} \quad (4)$$

where E_p and E_s are fields of the incident p- and s-polarized light and k is the wave vector in vacuum, which is equal to $2\pi/\lambda$, where λ is the wavelength. This field together with the additional field of polarized surface excites the tip, which in turn polarizes the surface producing noticed additional field, which in the present approximation is the field of the dipole image $P_{\text{im}\,i} = \pm K P_i$ situated at the distance $-z$ under the surface as a mirror image of the source. "+" corresponds to the transverse and "−" to longitudinal polarization as K is defined by (3). Self-consistent account of this mutual polarization gives the value of renormalized polarizability (2), and the dipole generated on the tip is not $P_i = \alpha E_i$ but $P_i = \alpha^* E_i$.

Finally, the total field at any point in the space is defined as the sum of external incident and reflected fields and fields generated by the dipole of the tip and its image in the surface. In the previous case [1], the tip dipole was constant; in this study, it depends on the illumination conditions and on the tip-surface separation.

The same parameters as in [1] were used for calculations, namely, silver tip mimicked by a sphere with radius 30 nm in front of gold surface, which is close to real experiment [8]. Now, the system is illuminated by the p- or s-polarized light of unit intensity. The angle of incidence is taken as 70°, which is close as to conditions of maximal exciting field what is proved later as to rather common experimental value. The ratio of fields at the tip and at the contacting surface, which depends on tip-surface separation, is shown in Figure 1, together with previous results for tip-source. As in the previous study, intensities in the case of s-polarization are very small, so results are shown for p-polarized light only.

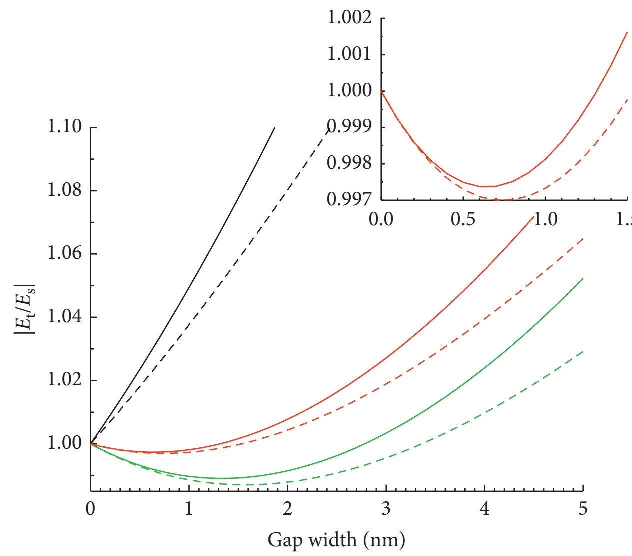

FIGURE 1: The ratio of fields at the tip apex and at the contacting surface for different substrate materials and wavelengths versus the tip-surface separation. Solid lines represent results for the tip source [1], and dashed lines represent results for the external illumination.

Dielectric functions of metals at different wavelengths were taken from [10], as for glass the refractive index was fixed to be $n = 1.5$.

As it is visible, external illumination slightly decreases the ratio of fields and shifts the minimum position from the surface for all used wavelengths and surfaces. In contrary to the tip-source case, we have additional free parameter in this study, namely, the angle of incidence. Its influence in the case of gold substrate and wavelength 632.8 nm is shown in Figure 2. Decreasing the angle of incidence decreases the calculated ratio of fields and shifts the minimum position further from the surface.

Such a behavior can be understood if to analyze the intensity of the external field at the surface and near it. Incident and reflected waves create an interference pattern perpendicularly to the surface. The period of this pattern at normal incidence is half of the wavelength and is inversely proportional to the cosine of the angle of incidence diverging at grazing incidence.

If the field has nodes at the surface of the ideal metal, as any field inside such a metal would create infinite current, it is not so strict for real metals with damping. The field of s-polarized light is rather low at the boundary, as the longitudinal field is constant across it due to the boundary

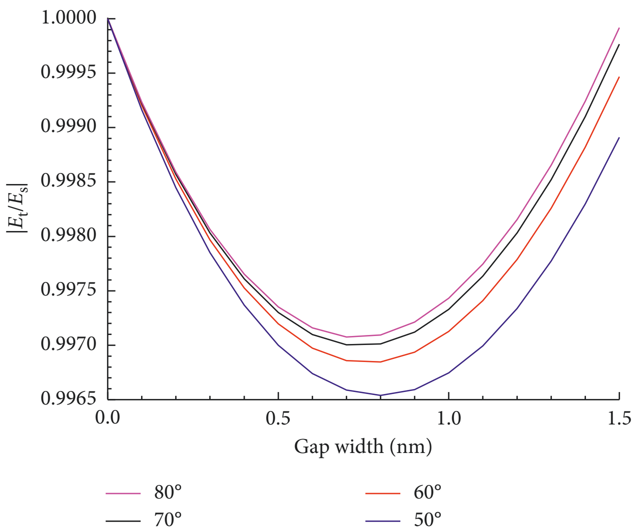

FIGURE 2: The influence of the angle of incidence on the ratio of fields at the tip apex and at the contacting surface.

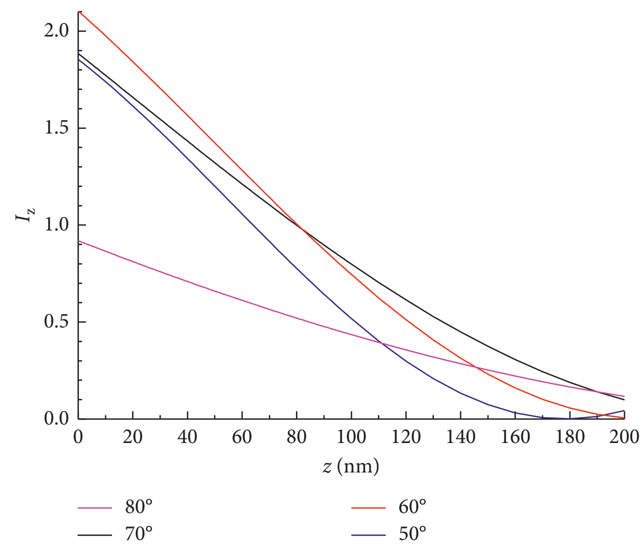

FIGURE 3: Intensity of the transverse field component versus the distance to a gold surface illuminated at different angles by p-polarized light with the wavelength of 632.8 nm.

conditions, but it is not necessary for p-polarized light. In this case not the field, but the displacement is constant across the surface for transverse field what remarkably decreases this field component inside metals with high value of dielectric function. But outside the metal, it may be noticeable. As a result, the low intensity of the longitudinal field has small rises at some proximity to the surface, but the intensity of the transverse field is higher at the surface and drops at some proximity for rather wide range of angles of incidence. The latter is shown in Figure 3.

The scenario of the interaction of the tip with the surface and the generation of the field distribution is the same as in the case of the tip-source considered earlier [1]. It is clear that, besides illuminating light, we have again only one source of the field, namely, excited tip. Also as in previous studies, the longitudinal field generates infinitesimal enhancement in the tip-surface gap for TERS configuration in comparison with the transverse field. The intensity of the incident p-polarized field in comparison with the highest field intensity between the tip and the surface calculated in the used simplest dipole model in Rayleigh approximation is less than 2% and even smaller if multipoles are taken into account. However, it is the incident field which excites the tip while tip-surface configuration serves only as an amplifier for this field. This scenario is supported by the angular behavior of the intensity of p-polarized light at the surface together with the intensity of the total field between the tip and surface at this illumination, which are shown on different scales in Figure 4. The maximum of those curves is slightly bigger than 60°, and the angle of the maximal enhanced intensity is a bit bigger than the angle of the maximal intensity of the field at the surface obtained from Fresnel equations by (4). Such a behavior completely coincides with the scenario proposed in [11] on the basis of exact calculations by the generalized field propagator technique.

However, approximation used in this study without taking into account multipoles is too coarse to calculate exact values of fields, and detailed discussion of obstacles of

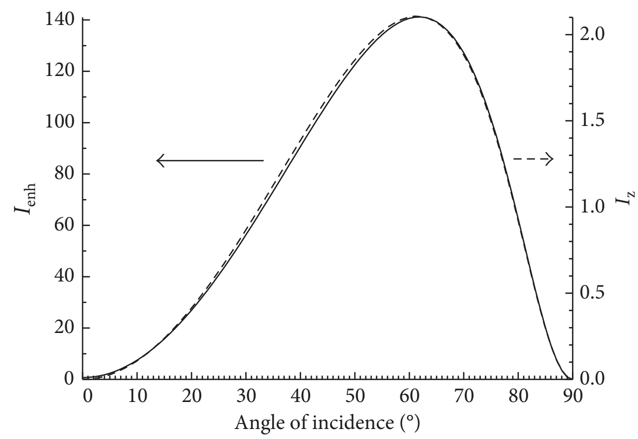

FIGURE 4: Angular dependencies of the intensity of the incident p-polarized light at the gold surface and the field enhanced by the touched sphere.

such an approach was given earlier [1], but it indicates qualitative behavior, which is proven by exact calculations [11]. Shown dependencies almost coincide being normalized and will completely coincide if it is drawing the angular dependency of the external field in the plane separated from the surface by the radius of the sphere. It is because the maximum of the total field shifts slightly to bigger angles along with increasing of tip-surface separation as the intensity of the external field at p-polarized illumination decreases with the distance to the surface faster at smaller angle of incidence, as shown in Figure 3. Just this decreasing of the p-polarized external field at tip retraction is exhibited in the shift of the minimum of the ratio of fields at the tip and at the surface further from the surface in comparison to the case of tip-source (Figure 1) and in the angular dependence of the position of this minimum, as external field decreases faster at smaller angles of incidence (Figure 2).

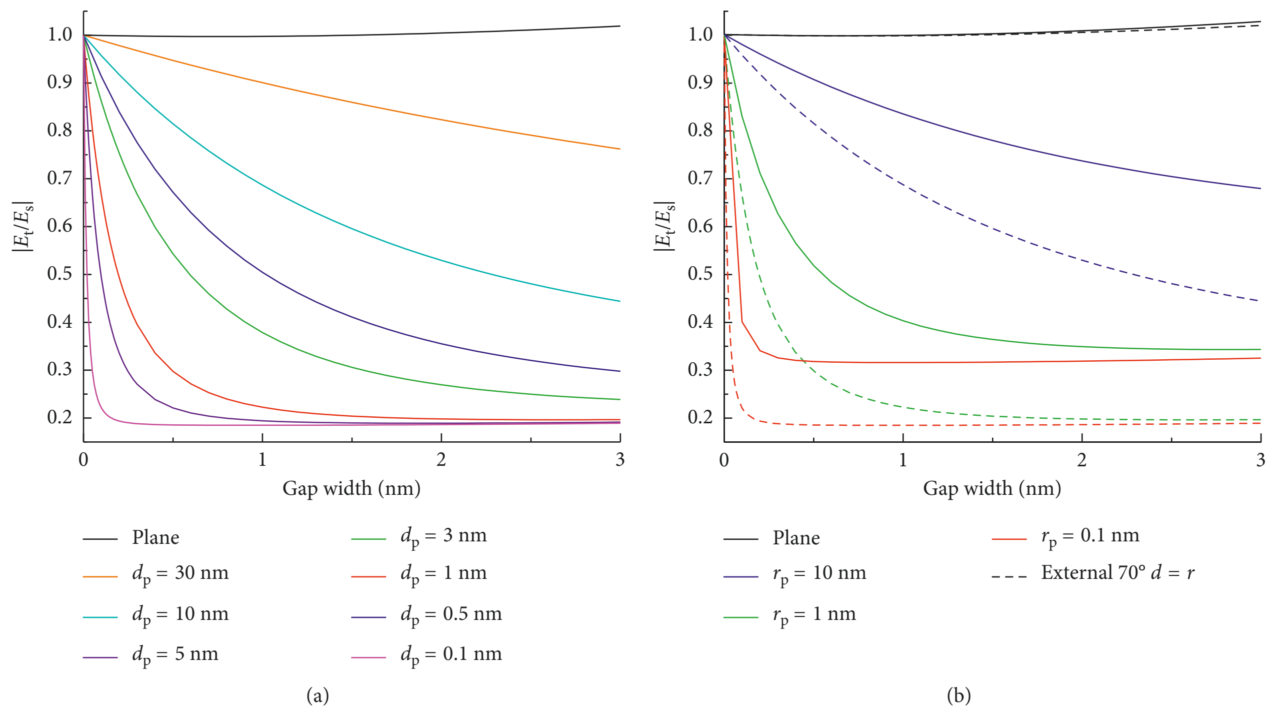

Figure 5: Dependencies of the ratio of fields at the tip apex and at the protrusion on the surface versus the distance between them for different sizes of the protrusion (a) and the comparison of the case of the external illumination with the case of tip-source [1] (b).

All these features support the conclusion that the tip-surface system is only the amplifier of the exciting field.

Moreover, this scenario is supported by numerical values of minima obtained in the case of tip-source [1] and external illumination in this study. For the shown case of the wavelength 632.8 nm and the angle of incidence 70°, values of minima differ about 0.0004 and the minimum for external illumination is about 0.75 nm as it is visible in Figure 1. At the same time, Figure 3 indicates that the transverse field at the angle of incidence 70° decreases with the speed of about 1.4/200 nm^{-1} or about 0.007 nm^{-1}; hence, at the separation of 0.75 nm, the external field is about 0.995 of the field at the surface. Considering that, in the used approximation, the external field is about 8-9 times less than that of the enhanced one, as shown in Figure 4, we can estimate the difference in the value of the minima for the two cases of excitation to be about 0.0005, which coincides with the presented modeling well.

It is clear that as the scenario of the field enhancement by the considered system does not depend on the method of the excitation, the account of multipoles as it was made earlier [1] would give the same result, namely, shallowing of the minimum and its shift to the origin. So, that modeling was not repeated for this case. Moreover, as the depth and the position of the minimum depend on the ratio of the tip radius to the tip-surface separation, decreased radius gives the described effect of the shallowing and shift of the minimum [1]. Inclusion of multipoles which were modeled by sequential account of images of the initial dipole at the surface and the tip effectively moves the summed dipoles generated at the tip to its apex [12]; thus, it works as effective decreasing of the tip radius. Such a behavior qualitatively describes what we can expect with more precise description of the problem taking into account multipoles.

It is necessary to note that the angular dependency of the field enhancement is defined purely by the angular dependency of the external exciting field at the surface, as the tip is considered close to the surface. Further tip-surface interaction and the final field enhancement do not depend on the angle of incidence. Different periods of the interference pattern would correct the angular dependence only with large separation of the tip and the surface, which is impractical in TERS.

3. Rough Surface

The structure of hemispherical protrusion on the surface used in the case of tip-source, as it has analytical solution for dipole model in Rayleigh approximation [13], is intractable for the case of external illumination due to complex expressions for the polarizability of the hemisphere [14, 15]. Thus, for the case of external illumination, a feature on the surface was modeled by additional spherical particle on the surface. From the first point of view, this model has principal difference from the case of the tip-source, as incident light excites both spheres in contrary to the one field source [1]. However, the dipole moment of a particle is proportional to its volume, so for small protrusions the field in the other space generated by a small sphere on the surface would be small in comparison to the field from the tip. However, its influence will be noticeable at the top of such a protrusion due to scaling of fields in Rayleigh approximation. The scaling can be easily demonstrated if to take into account that the value of the dipole generated on a sphere by the external field is proportional to the volume of the sphere i.e. to the third power of its radius R^3. At the same time the strongest field component in Rayleigh approximation decreases reversely proportional to the same third power of the distance R^{-3}. As a result, the field on the surface of the sphere does not depend on its radius in Rayleigh (static) approximation.

In the considered approach, we have two spherical particles, which reproduce the tip and protrusion. Together with their images in the surface, we obtain the system of four dipoles with mutual interactions. In spite of this system being nonlocal, that is, the field at any point depends on the field at two centers of spheres, it is rather easy to obtain the expression for the dipole moment of any sphere:

$$P_{ti} = \alpha_{ti}^{*} \frac{E_{0ti} + \alpha_{pi}^{*} G_i E_{0pi}}{1 - \alpha_{pi}^{*} \alpha_{ti}^{*} G_i^2}, \tag{5}$$

where E_0 is the external field at the tip t or protrusion p for i—longitudinal or transverse direction to the surface. Dipole moment of the sphere modeling protrusion is obtained by the exchange of indices t and p. Self-consistent polarizability α^* is given by expression (2).

The propagator G in Rayleigh approximation is

$$G_i = \left(z_t - z_p\right)^{-3} \pm K\left(z_t + z_p\right)^{-3}, \tag{6}$$

where "+" is used for transverse and "−" for longitudinal fields. K is given by (3).

After obtaining dipole moments of the tip and protrusion, the calculation of the field at any point of the system is straightforward, that is, the sum of the external field (incident and reflected ones) and fields of four dipoles (two dipoles of spheres and their images in the surface).

Figure 5(a) demonstrates the ratio of fields at closest points of both spheres situated one over another at one vertical and illuminated at the angle of incidence of 70°. As in the previous study, the radius of the silver tip is taken as 30 nm, as the surface and protrusion are considered as made from gold and the radius of the sphere mimicking protrusion varies. Figure 5(b) gives the comparison of the external illumination of the present case with the case of tip-source obtained in [1].

The dependencies shown in Figure 5 of the field ratios are qualitatively the same as were obtained for the tip-source but drop noticeably faster than for the case of hemispheres with the radius equal to the diameter of the sphere on the surface. It can be explained by two moments. In the first, the sphere on the surface obtains its own dipole moment from the illumination, which generates its own field and its value is not small just on the surface of this sphere because of noticed scaling. In the second, due to decreasing of the external field at some distance from the surface shown in Figure 3, the tip is excited by slightly weaker field than the protrusion. The latter reason is minor correction but should be noticed for the sake of completeness. As a result, the field at the protrusion is higher and the field at the tip is smaller with external illumination than for the case of tip-source, and the ratio of fields drops faster.

By increasing the size of the protrusion, one can obtain remarkable difference from the case of tip-source. For instance, if the diameter of the sphere on the surface is 100 nm, the dependency of the ratio demonstrates small maximum instead of the minimum on the shown length scale. However, calculations for big values cannot be considered as exact even for the chosen formalism, as particle-particle interaction is calculated without taking into account the phase change of fields but the phase change of the external field is taken into account. Figure 5 demonstrates ratios for the diameter of the sphere on the surface not bigger than 30 nm.

4. Conclusions

Simple dipole approximation was applied to the analysis of the ratio of fields generated at the tip apex and the contacting surface. Results were analyzed for the standard for TERS configuration with external illumination. Comparison of the obtained results with the distribution of the external field of the illuminating light reveals the origin of the obtained angular and distance dependencies. It demonstrates that the tip-surface system is only the amplifier of the external field given by the interference of the incident and reflected waves. Comparison of the present results with the results obtained earlier for the case of tip-source proves made conclusions and demonstrates stronger field at the rough surface due to its direct excitation by the external field which generates two sources of fields polarizing the whole system in contrary to the case of the only tip-source in previous consideration.

Data Availability

No data were used to support this study.

Conflicts of Interest

The author declares that there are no conflicts of interest.

References

[1] E. Bortchagovsky, "Simple modeling of the ratio of fields at a tip and at contacting surface," *Nanospectroscopy*, vol. 2, no. 1, pp. 7–14, 2016.

[2] E. G. Bortchagovsky and U. C. Fischer, "A tetrahedral tip as a probe for tip-enhanced Raman scattering and as a near-field Raman probe," *Journal of Raman Spectroscopy*, vol. 40, no. 10, pp. 1386–1391, 2009.

[3] E. G. Bortchagovsky, S. Klein, and U. C. Fischer, "Surface plasmon mediated tip enhanced Raman scattering," *Applied Physics Letters*, vol. 94, no. 6, article 063118, 2009.

[4] C. Ropers, C. C. Neacsu, T. Elsaesser, M. Albrecht, M. B. Raschke, and C. Lienau, "Grating-coupling of surface plasmons onto metallic tips: a nanoconfined light source," *Nano Letters*, vol. 7, no. 9, pp. 2784–2788, 2007.

[5] H. G. Frey, S. Witt, K. Felderer, and R. Guckenberger, "High-resolution imaging of single fluorescent molecules with the optical near-field of a metal tip," *Physical Review Letters*, vol. 93, no. 20, article 200801, 2004.

[6] T. H. Taminiau, R. J. Moerland, F. B. Segerink, L. Kuipers, and N. F. van Hulst, "λ/4 resonance of an optical monopole antenna probed by single molecule fluorescence," *Nano Letters*, vol. 7, no. 1, pp. 28–33, 2007.

[7] E. G. Bortchagovsky and U. C. Fischer, "The concept of a near field Raman probe," *Nanoscale*, vol. 4, no. 3, pp. 885–889, 2012.

[8] E. G. Bortchagovsky, T. Schmid, and R. Zenobi, "Internal standard for tip-enhanced Raman spectroscopy," *Applied Physics Letters*, vol. 103, no. 4, article 043111, 2013.

[9] J. D. Jackson, *Classical Electrodynamics*, John Wiley & Sons, Hoboken, NJ, USA, 1962.

[10] P. B. Johnson and R. W. Christy, "Optical constants of the noble metals," *Physical Review B*, vol. 6, no. 12, pp. 4370–4379, 1972.

[11] O. J. F. Martin and C. Girard, "Controlling and tuning strong optical field gradients at a local probe microscope tip apex," *Applied Physics Letters*, vol. 70, no. 6, pp. 705–707, 1997.

[12] L. Brus, "Noble metal nanocrystals: plasmon electron transfer photochemistry and single-molecule Raman spectroscopy," *Accounts of Chemical Research*, vol. 41, no. 12, pp. 1742–1749, 2008.

[13] D. V. Sivukhin, The Course of General Physics, Electricity, Vol. 3, Nauka, Moscow, Russia, 1996, in Russian.

[14] M. M. Wind, J. Vlieger, and D. Bedeaux, "The polarizability of a truncated sphere on a substrate I," *Physica A: Statistical Mechanics and its Applications*, vol. 141, no. 1, pp. 33–57, 1987.

[15] H. Kettunen, H. Wallén, and A. Sihvola, "Polarizability of a dielectric hemisphere," *Journal of Applied Physics*, vol. 102, no. 4, article 044105, 2007.