Effects of a silicon probe on gold nanoparticles on glass under evanescent illumination

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Abstract: We have numerically investigated the influence of a nanoscale silicon tip in proximity to an illuminated gold nanoparticle. We describe how the position of the high-permittivity tip and the size of the nanoparticle impact the absorption, peak electric field and surface plasmon resonance wavelength under different illumination conditions. We detail the finite element method (FEM) approach we have used, whereby we specify a volume excitation field analytically and calculate the difference between this source field and the total field (i.e., scattered-field formulation). We show that a nanoparticle tip can locally enhance the absorption of the particle as well as the peak electric field at length scales far smaller than the wavelength of the incident light.

References and links

1. Introduction

There have been many studies of the optical behavior of metal nanoparticles under different conditions. Motivating applications range from communications, computing, and data storage to medical diagnostics and therapies. The enhanced absorption, scattering, and electric fields associated with the localized surface-plasmon resonances (LSPRs) of metal nanoparticles find application in information processing [1], sensing [2], microscopy [3,4,10] and lithography [5,6], materials processing [3–5] and photovoltaics [6]. In many of these applications, nanoparticles are immobilized on substrates that strongly influence their optical behavior [7,8]. In addition, several studies have been conducted of the optical properties of nanoscale probes or tips [9–11]. These have largely addressed applications in near-field microscopy and enhanced Raman scattering [12,13], and have focused on metal or metal-coated tips. Our recent work using a nanoscale tip to locally modify nanoparticles [3] prompted us to study the behavior of a nanoscale tip in proximity to a metal nanoparticle on a substrate.

Although this geometry is frequently encountered, there have been only a few reports describing the optical phenomenon associated with a tip near a particle. Fikri et al. conducted 2D finite element simulations of scanning probe/particle geometries to study the effect of probe vibration and lock-in detection on scanning near-field optical microscopy [14]. Chen et al. studied the operation of Apertureless Scanning Near-Field Optical Microscopy (aSNOM) both experimentally and numerically for gold nanostructures on a silicon surface [15]. Esteban et al. simulated the achievable resolution and contrast of aSNOM by phase and amplitude imaging process using a gold particle embedded in a glass substrate and illuminated from above at a fixed wavelength [16]. In other work, Stiles et al. experimentally studied the effect of a standard AFM tip on optical scattering from nanoparticles [17]. Most recently Sadiq et al. investigated a system in which nanoparticles were probed with a metallic, grating-coupled near-field optical probe [18]. Although highly informative, these papers do not address the absorption and field enhancement associated with the geometry of interest here, i.e. a simple high-dielectric-constant tip near a nanoparticle resting on a substrate and illuminated using total internal reflection over a range of wavelengths. In addition to the intrinsic interest of this geometry, this configuration also required addressing several simulation challenges, which should prove useful in addressing a broad range of nanoscale optical problems via the finite element method (FEM).
In this paper, we explored how a nanoscale probe made of a high-permittivity material such as silicon (Si) affects the absorption cross-section ($C_{abs}$) and electric-field enhancement of spherical gold nanoparticles (AuNP) of different sizes resting on a BK7 glass substrate. The simulated geometry is shown in Fig. 1. Illumination is from below under total internal reflection (TIR) conditions. We considered both transverse electric (TE) and transverse magnetic (TM) excitations, and we varied the position of the Si tip both laterally and vertically with respect to the AuNP. The effect of the tip can be viewed from two perspectives. First, even in the absence of a particle, light will evanescently couple, or optically tunnel, from the substrate to the high-permittivity tip. Second, the tip strongly perturbs the local dielectric environment of the NP. In both cases, one expects the presence of the tip to enhance absorption and scattering for the NP and to enhance the local electric field in the tip-NP gap. Moreover, one would expect the spatial localization of these near-field effects to be governed primarily by the geometry and not to be limited by the wavelength of illumination. The dielectric tip allows us to study these effects without introducing additional complexity associated with the LSPRs of a metal or metal-coated tip. Enhanced understanding of these effects will lead to better control of selective absorption and field enhancement, with possible applications in deterministic patterning, sensing and imaging.

![Fig. 1](image_url)

2. Simulation

We used COMSOL Multiphysics 3.5a [19] with the RF module to implement the finite element method. COMSOL’s 3D scattered harmonic propagation mode calculates the difference between a volume source field defined in the absence of a scatterer and the total field in the presence of the scatterer. This difference is referred to as the scattered field, which still provides access to the details of the near field and should not be confused with techniques for calculating the scattered far field. We defined the source field as a plane wave of wavelength between 450 and 650 nm. The wave is incident from within the substrate at a supercritical angle (50° from the normal to the substrate surface). The source field was defined analytically, using the Fresnel equations, over the entire 3D simulation domain, excluding the perfectly matched layers (PML), as if the NP and tip were absent. For TE simulations the source field was specified in terms of $E_z$, while for TM simulations the source field was specified by $E_x$ and $E_y$. 
Others have used a similar approach in which a volume source field was defined by launching a plane wave from a boundary in a simulation without the scatterer and substituting the resulting total field as the source field in a second simulation, which is otherwise identical to the first but for the explicit presence of the scatterer [7]. Our approach has two key advantages: (1) by defining the volume source field, we can eliminate unphysical diffractive effects associated with launching a plane wave from a truncated boundary or from using unrealistic periodic boundary conditions; and (2) by defining the source field analytically, we can use a single finite-element simulation to calculate the final scattered field.

Our 600-nm-radius spherical simulation domain is divided into two hemispherical half-spaces (Fig. 1(b)). The lower geometry is the substrate, BK7-type glass, and the upper is air (vacuum). The domain is surrounded by a 100-nm-thick perfectly matched layer (PML) backed by scattering boundaries to prevent spurious reflections. The perfectly matched layers are chosen to match the index of refraction in the adjacent domain, either air or glass. A 50-nm-diameter AuNP is placed in contact with the substrate at a single point. In reality, NPs typically contact substrates along a crystal facet; however, simulation of all the varieties of such an interface was impractical for this study. Nevertheless, we did take the precaution of limiting our search for the maximum electric-field enhancement to a rectangular region surrounding the upper hemisphere of the NP. This eliminates any spurious field peaks at the point contact. The refractive index values for BK7 glass were taken from the Schott catalog [20], while the values for gold were taken from Johnson and Christy [21].

The Si tip radius was 10 nm and the cone angle was 10° at the apex, based on the nominal dimensions of a typical probe used in atomic force microscopy (AFM) [22]. The refractive index of Si was taken from measurements compiled by J. A. Woolam, Inc. and the University of Nebraska, which are very similar to the data given by Palik [23]. In the simulation, the tip length was truncated to 370 nm. While extending the tip through the PML would have approximated a more realistic structure (several microns in length), the scattered-field formulation in COMSOL assumes that the scattering objects are entirely confined within the physical domain. Illuminating at normal incidence produces a strongly guided wave in the Si tip. And so the choice of tip length can significantly affect the simulation results. Loke and Mengüç have also explored the effect of tip truncation using a newly developed Discrete Dipole Approximation with Surface Interaction analysis [5]. However, in our case, the wave guiding effect is far weaker because we illuminate at oblique incidence beyond the critical angle. Because the evanescent wave decays exponentially, by the upper end of the tip length the norm of the electric field \( (\sqrt{E_x E_x + E_y E_y + E_z E_z}) \) is reduced to around 3% of the source field amplitude. In TIR illumination changing the tip length from 370 nm to 670 nm causes no more than 3.4% difference in \( C_{abs} \). The gap between the tip and PML was 100 nm or approximately one fifth of a wavelength. This choice of gap allows the mesh elements to remain approximately the same size as in the surrounding air region, and thus has minimal impact on computation time.

The vertical and lateral positions of the tip were varied over a range of 1 to 100 nm and ±320 nm, respectively. For all the simulations described here we used a single plane of symmetry to reduce computation time. The same geometry was used for all simulations in order to ensure consistent meshing. Therefore, to model a suspended particle in free space, we defined every subdomain with refractive index of unity except for the AuNP. Likewise, for simulations without the tip, the tip subdomain was defined with refractive index 1. The AuNP had 359 mesh elements and the maximum element sizes in the tip, PML and remaining subdomains were 50 nm, 150 nm and 75 nm respectively. These parameters were optimized to run a single-wavelength simulation using dual Intel Xeon quad-core processors (2.27 GHz and 24GB RAM) in 128 s. Although we had only one element between the tip and particle, inserting 1000 elements instead of 1 did not change the \( C_{abs} \) of AuNP more than 1%. Reducing the maximum element size from 75 nm to 50 nm in the substrate and air domains...
reduced the error compared to Mie theory from 5% to only 2% but required 27 times longer simulations.

3. Validation

We first compared our FEM results with the Lorenz-Mie theory [24] for a 50-nm-diameter AuNP surrounded by air ($n = 1$). The absorption cross-section was calculated for both TE and TM waves (defined with respect to the symmetry plane but physically indistinguishable). Over the wavelength range from 450 to 650 nm, the largest deviation between the analytical and FEM absorption cross-sections was 5%, as shown in Fig. 2(a). Secondly, we ran the simulation with the lower half-space as BK7 but without any scatterer in the simulation domain. In this case, any non-zero scattered field results from numerical errors or unphysical reflections from the boundaries. In this case, the maximum norm of the scattered field was found to be three orders of magnitude lower than the source field, while the average norm was four orders of magnitude lower.

The geometry, with or without a tip, is azimuthally symmetric, provided the tip is not laterally offset with respect to the NP. For normally incident illumination, there is no physical difference between TE and TM waves; however, the electric field is oriented differently with respect to the symmetry plane. Thus, it is important to confirm that the polarization of the normally incident wave does not significantly affect the results. In fact, with only a particle on the substrate (tip being absent), $C_{abs}$ of the AuNP at normal incidence differed by no more than 0.2% between TE and TM simulations in the 450-650 nm wavelength range.

![Fig. 2. (a) Validation against Lorenz-Mie theory at 60° angle of incidence for both TM and TE polarization (physically indistinguishable but numerically implemented using distinct equations and symmetry conditions). The worst-case error in $C_{abs}$ is below 5%. (b) Effect of tip proximity on $C_{abs}$ of AuNP at 532 nm. For TM illumination with a relatively large electric-field component along the tip axis, absorption increases rapidly as the tip approaches the NP. For TE illumination, the tip has little effect. (c) Under TE illumination, the increase and redshift of $C_{abs}$ is due to the substrate only and varying the tip-NP vertical separation has little effect. As a result, all the curves overlap. (d) Under TM illumination, $C_{abs}$ increases and the resonance wavelength redshifts by 5 nm as the tip approaches the AuNP. In all cases the y-axis scales were kept the same to allow direct comparison. The black vertical lines in (a), (c) and (d) indicate the resonant wavelength of a 50-nm-diameter AuNP in free space.](image)

Convergence of the calculations for the entire geometry (tip, particle, and substrate) was examined by enlarging the domain from 600 nm to 1400 nm radius in steps of 200 nm, for
each polarization at 60° angle of incidence. $C_{abs}$ in AuNP changed by less than 0.6% for any given step in the domain size.

4. Effects of Si tip on AuNP absorption and field enhancement

It is well established that $C_{abs}$ near the LSPR of nanoparticles increases as the permittivity of the surrounding media increases. The peak absorption wavelength also redshifts as the energy associated with the plasmon resonance decreases in the more strongly polarizable environment [25]. As a result, the presence of the substrate alone causes a small increase and baseline redshift in the absorption resonance with respect to the particle in free space [26]. Comparing Fig. 2(a), the free-space result, with the “No tip” cases in Fig. 2(c) and (d) shows this clearly. More importantly, the high dielectric constant of the Si tip can strongly modulate $C_{abs}$ of the AuNP. Figure 2(b) plots the absorption cross-section as a function of tip-NP separation at a fixed wavelength of 532 nm. Simulations were conducted down to 1-nm separation; however, it has been established that classical electromagnetic analysis is insufficient to accurately quantify interactions at these length scales [27]. The data point for a 1-nm gap is thus included as a reference for future comparison with coupled electromagnetic and quantum-mechanical simulations.

For the TE case the electric field is polarized transverse to the tip-NP axis and the tip has little effect on particle absorption, even at separations approaching 1 nm. Likewise, Fig. 2(c) indicates that the absorption spectrum does not change significantly with tip-NP separation. This is expected, since the surface charge distribution and hence the electric field are concentrated at the sides of the NP, and away from the tip. As a result, the tip is only a weak perturbation and does not dramatically affect $C_{abs}$. In contrast, for TM illumination, the electric field is partially polarized along the tip-NP axis. In this case, charge is concentrated at the top and bottom of the AuNP, as well as at the apex of the Si tip, and the tip strongly perturbs the electric field around the AuNP. As the vertical distance between tip and NP decreases, the increasing polarization of the high-permittivity tip reduces the resonant frequency of the configuration [26] and leads to a longer resonance wavelength. As can be seen in Fig. 2(b) and (d), the absorption and resonance wavelength increase and redshift, respectively, as the tip approaches the particle.

We also investigated the dependence of absorption on lateral separation between the tip and the particle. In this case the separation is parallel to the substrate-air interface as depicted in Fig. 1(a). In order to simplify the simulation setup, the AuNP, rather than the Si tip, was moved in the simulation domain. A positive number indicates that the tip is to the left of the particle according to the view in Fig. 1(a). The vertical separation is kept constant at 5 nm. As the tip is brought closer to the NP laterally, $C_{abs}$ is enhanced (Fig. 3(a)) under TM illumination. The maximum absorption occurs when the tip is located 5 nm to the left of the particle. Asymmetry in the relationship between $C_{abs}$ and lateral position is not surprising given the asymmetric illumination. We attribute the lower, broader peak at separations near ~150 nm, which occurs when the tip is to the right of the particle, to interference effects resulting from reflection and scattering from the tip when the tip-particle separation is approximately $\lambda/4$. Once again, the tip has little effect for TE illumination. Importantly, the absorption enhancement is spatially localized at the scale of the tip-apex-NP geometry, not the wavelength of the incident light. As a result, NPs can be selectively targeted for modification, sensing, or processing at a scale far below the diffraction limit.
In addition to considering the integrated absorption of the AuNP, we also investigated the maximum field enhancement. These data were sampled at 115351 points in the upper half of the AuNP to find the maximum field, since the maximum field occurs at various positions around the particle surface depending on the lateral displacement of the Si tip with respect to the AuNP. Figure 3(b) plots the field enhancement observed at the top surface of the particle. In this case, the localization of the field enhancement is even more pronounced than the corresponding effect for $C_{\text{abs}}$ (Fig. 3(a)). As the tip moves across the top of the AuNP, both the vertical and horizontal gaps between the tip surface and the metal surface are reduced. Thus, the enhancement rapidly increases and is localized with a full-width at half-maximum of 40 nm.

Figure 4 plots the maximum field enhancement as a function of vertical separation between the tip and the particle. Exponential decay of the field enhancement as a function of increasing distance between a tungsten tip and a Si substrate was recently shown by Chen and Wang [10]. Our tip dimensions were similar to their optimum tip geometry, though we used a Si tip and glass substrate. One would not expect a purely exponential dependence for the substrate-NP-tip case, but Fig. 4(a) shows a similar rapid decrease in field as Ref [10], with an even larger field enhancement. As mentioned earlier, we did not take into account quantum-mechanical effects in our simulations. With tip-NP gaps of 1 nm or less, the purely classical approach leads to a monotonic increase in the field enhancement, yet tunneling effects may very well modify the optical response and reduce the electric-field enhancement at such small separations [27]. Again for TE polarization, the tip has little effect.
Other geometrical parameters affect absorption and field enhancement as well, in particular the relationship between tip radius and particle size. Thus, we simulated the absorption enhancement for particles with diameters ranging from 10 nm to 50 nm located 5-nm below the same silicon tip at 532 nm incident wavelength. The absorption efficiency, \( Q_{\text{abs}} = C_{\text{abs}}/(\pi r^2) \), is plotted in Fig. 5. For a particle much smaller than the incident wavelength, \( C_{\text{abs}} \) is proportional to the radius cubed [25]; thus, an approximately linear increase in the absorption efficiency \( Q_{\text{abs}} \) as a function of diameter is expected. This can be seen in Fig. 5 for both the TE and TM cases in the absence of the tip. In the TE case, the presence of the tip does not dramatically alter the absorption of the particle. For TM illumination, the tip-induced enhancement in \( Q_{\text{abs}} \) is significant. The greatest enhancement in absorption efficiency is observed when the radius of the particle is smaller than the radius of the tip. This is not surprising because in this case the tip provides a strong perturbation on the local dielectric environment of the particle. As the particle radius becomes larger than the tip radius, the absorption enhancement lessens, as can be seen by the convergence of the “TM with tip” and “TM without tip” curves in Fig. 5. Thus, to selectively target particles for modification using a nanoscale tip, one must balance absorption enhancement, which requires a large tip-radius to particle-radius ratio, with spatial selectivity, which requires a smaller tip radius. Future multi-particle simulations are required to quantify this tradeoff.
5. Conclusions

In this study, we have explored the effect of a nanoscale tip on the absorption and field enhancement for a metallic nanoparticle illuminated under TIR conditions. For an electric field polarized orthogonal to the tip axis little effect is observed. If the electric field is partially polarized along the tip axis, then both absorption and electric fields are strongly enhanced. The enhancement is accompanied by a redshift in the surface-plasmon resonance wavelength of the particle. These effects are observed when the vertical and horizontal separation of the tip and nanoparticle are significantly less than the wavelength of the illuminating light. Thus, the technique can be used to selectively excite nanoparticles, and thus drive modification processes, far below the diffraction limit. The changes in absorption and field enhancement with particle size indicate that there is likely to be a tradeoff between spatial localization of these effects and their maximum enhancement. Further studies are required to better understand this tradeoff; however, the 3D simulations presented here already improve the understanding of tip-particle interactions and should influence applications including tip-based nanomanufacturing, imaging, and sensing.

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