Plasmonic near-field probes: a comparison of the campanile geometry with other sharp tips

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Abstract: Efficient conversion of photonic to plasmonic energy is important for nano-optical applications, particularly imaging and spectroscopy. Recently a new generation of photonic/plasmonic transducers, the 'campanile' probes, has been developed that overcomes many shortcomings of previous near-field probes by efficiently merging broadband field enhancement with bidirectional coupling of far- to nearfield electromagnetic modes. In this work we compare the properties of the campanile structure with those of current NSOM tips using finite element simulations. Field confinement, enhancement, and polarization near the apex of the probe are evaluated relative to local fields created by conical tapered tips in vacuum and in tip-substrate gap mode. We show that the campanile design has similar field enhancement and bandwidth capabilities as those of ultra-sharp metallized tips, but without the substrate and sample restrictions inherent in the tip-surface gap mode operation often required by those tips. In addition, we show for the first time that this campanile probe structure also significantly enhances the radiative rate of any dipole emitter located near the probe apex, quantifying the enhanced decay rate and demonstrating that over 90% of the light radiated by the emitter is "captured" by this probe. This is equivalent to collecting the light from a solid angle of ~3.6 pi. These advantages are crucial for performing techniques such as Raman and IR spectroscopy, white-light nanoellipsometry and ultrafast pump-probe studies at the nanoscale.

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Introduction

The design of advanced nanostructured materials can benefit from spectroscopic characterization techniques that provide chemical information with nanoscale spatial resolution. In principle, optical near-field investigations can access this parameter space, but despite offering optical imaging and spectroscopy capabilities with sub-diffraction-limited resolution [1-8], the general applicability of near-field microscopy has been limited by the far-field to near-field coupling properties of its probes. A novel near-field probe structure [9, 10] – known as the "campanile" geometry – based on a design originally proposed by Staffaroni and Yablonovitch [11] has recently been shown to enable multidimensional nanospectroscopic imaging of nanostructures without many of the constraints and limitations encountered by previous near-field probes [9]. To better understand the capabilities of the campanile probe geometry, it is important to compare its optical properties with those of other near-field probes, which is the main focus of this paper.

An ideal near-field probe should possess nanoscale resolution, efficient far-field to near-field coupling, strong local field enhancement, and perhaps most importantly, reproducibility and robustness. In addition, such a probe should provide background-free operation, control over near-field polarization, and operate over a wide range of frequencies (i.e. – it should be broadband rather than resonant). Compatibility with existing instrumentation would also be desirable. Conventional aperture-based near-field scanning optical microscopy (NSOM) tips are lacking in a number of these categories. This, combined with the increased need to characterize materials at nm length scales, has led in recent years to a number of approaches aimed at improving one or more of these desired near-field probe properties.

One such approach, termed apertureless NSOM (a-NSOM), uses the apex of a sharp tip as either a local field scatterer or as a locally-enhanced optical source [12–17]. In either case, spatial resolution is determined by the radius of curvature of the tip, which is typically $10\sim 20$

nm [7, 18–25]. It is also well-known from surface-enhanced Raman spectroscopy (SERS) that nanoplasmonic fields are strongest in nanogap-like regions between plasmonically-coupled structures [18, 26–29]. Therefore, some of the largest signals in a-NSOM originate from tips exhibiting surface roughness and a SERS-like "hot-spot" at the apex [30]. But although the surface roughness enhances both light-surface plasmon polariton (SPP) coupling efficiency and local fields in hot-spots, the random nature of the roughness leads to performance that is extremely variable and not reproducible. To better exploit the additional enhancement resulting from the small gaps in coupled plasmonic structures, tip-enhanced Raman scattering (TERS) methods based on the so-called "tip-substrate gap mode" geometry have been developed. In the tip-substrate gap mode, a sharp metal tip is held ~1nm above a metallic substrate, with the sample located in the gap, effectively forming a three-dimensional (3D) vertically-oriented coupled dipole- or bowtie-like plasmonic antenna [25, 31–36].

In practice, however, the operational requirements of tip-substrate gap mode in a-NSOM limit its general applicability. It requires both a metallic substrate and a very small tip-substrate gap, meaning only very thin samples (e.g. molecular monolayers) can be investigated. Also, the highest enhancements can be achieved only when the light is polarized in the "z" direction normal to the sample surface.

A solution to these limitations is to engineer coupled optical antenna structures [37, 38], i.e. – optical antennas with a small gap [39], directly on the scan-probe tip [40, 41]. However, these probes are, by design, resonant structures: enhancement and throughput is large only for a small wavelength range. This is also true for probes based on extraordinary optical transmission [42, 43] and antenna apertures [44, 45]. Ideally, enhancement should be large over a wide spectral range for optimized spectroscopic measurements.

The desire to achieve large near-field enhancement over many wavelengths while operating in a background-free excitation modality has led researchers to adopt novel nanofocusing strategies based on the broadband adiabatic propagation and compression of SPP modes on a conically tapered tip. These strategies combine elements of the previously mentioned a-NSOM tips, which also utilized the adiabatic taper for near-field enhancement, with efficient photon-to-plasmon coupling structures that can be illuminated far from the sample, launching a plasmon wave towards the tip apex and avoiding most unwanted background excitation. For example, grating couplers were fabricated a few microns up the conical adiabatic taper (CAT) tip shaft [46-48], leading to far-field to near-field coupling efficiencies of $\sim 2\%$ -4%. Though grating couplers are narrow-band by design, Raschke and associates have successfully "chirped" the grating spacing within the far-field illumination area to enable SPP coupling over a relatively broad wavelength range. Another example is the probe geometry described in [49], where a photonic crystal fabricated on a cantilever is used to capture and convert light to plasmons propagating adiabatically on a sharp cone located at the center of the photonic crystal cavity. Although these photonic crystals are also narrowband couplers, it is conceivable that more complex designs (e.g. fractal-based structures) could allow for coupling over a greater number of wavelengths.

These types of probes represent a significant step forward, as they efficiently integrate the concepts of broadband photon-to-plasmon couplers, plasmonic waveguides, and optical antennas. They have recently demonstrated large TERS enhancements from a number of different samples including molecular monolayers [50] and silicon nanocrystals [49]. However, there is one primary drawback to these CAT tips: for realistic tip radii of curvature, maximum enhancement is still only achieved in the tip-substrate gap mode. Thus, the question remains: is it possible to realize the best properties of these CAT tips in a structure that moves beyond this limitation?

It is in this context that we proposed the photonic-plasmonic hybrid NSOM probe termed the "campanile" tip, so-called due to its resemblance to bell towers of the same name [9]. These campanile tips couple the photonic to the plasmonic field, then adiabatically compress the plasmon mode over a broad bandwidth. The confinement of the optical near field is determined by the gap size between the two antenna arms, which can be well below 10nm given the appropriate resolution of the dielectric deposition method. Based on excitation through the back of the tip similar to traditional aperture-based NSOM tips, the campanile tips enable nearly background-free nanoscale imaging and spectroscopy, even on dielectric, non-transparent substrates.

In this work we used FEM to simulate state-of-the-art adiabatic-compression-type probes, and compare it with the campanile tip geometry. Understanding the relative strengths and weaknesses of each NSOM probe geometry ultimately helps in designing probes with superior field coupling, enhancement and resolution capabilities.

Results and discussion

Perhaps still the most common near-field imaging modality is the aperture-based NSOM, with the probes consisting of metal-coated tapered dielectric structures with a resolution-defining sub-wavelength aperture at the apex [3, 51–57]. While this geometry is "background-free", the boundary conditions for this type of optical waveguide demand that all propagating modes within the taper get cut off before reaching the aperture, causing only evanescent waves to leak out from the end, which results in low optical throughput and signal strength [1, 58]. In addition, maximum probe input intensity is limited by thermal damage to the metal film in the taper region. Because throughput is inversely proportional to the fourth power of the aperture radius, signal-to-noise considerations in NSOM ultimately constrain aperture size, and resolution, to \sim 50 – 100 nm.



Fig. 1. (a) 3D schematic of a campanile structure at the end of a gold-coated conical tapered NSOM fiber. A diagram of a metal-insulating-metal (MIM) structure is shown in the inset.(b) FEM simulations of a campanile structure with a final gap size $D_o = 10$ nm and a round corner radius of 4 nm; $\lambda = 713$ nm was used here. The yz-section of the spatial profile of the steady-state electric field amplitude near the end of the campanile, normalized to he amplitude of the incident field and a geometric factor [9]. The white arrows indicate the polarization of the electric field. The simulation shows an 8% reduction in enhancement relative to the simulation in reference [9] with no rounding at the corners at the gap.

To get past the cut-off mode problem one can turn to a metal-insulator-metal (MIM) waveguide geometry (Fig. 1(a) inset). It is well-known that the symmetric SPP mode in a metal-insulator-metal (MIM) waveguide is supported without any cut-off frequency [59] no matter how thin the insulating layer. A linearly tapered MIM structure provides one of the simplest methods for overcoming the diffraction limit and has been utilized extensively at longer wavelengths, in the microwave [59] and terahertz regimes [60, 61]. As the thickness D of the dielectric layer decreases, higher order modes are cut off, until only the fundamental plasmonic mode is allowed to propagate (the tapered MIM waveguide effectively acts as mode filter). In addition, the fundamental mode's propagation constant increases as D decreases. Therefore, the SPP wavelength decreases as the structure is tapered down,

analogous to the tapered adiabatic compression described previously [47, 62, 63]. It has been demonstrated that efficient delivery of light to an ultra-small region is possible in 2D space using a tapered planar MIM structure [64–69], and in 3D space with an MIM dimple lens structure [70], which is similar to the campanile geometry. When a linearly tapered MIM structure with an optimal taper angle is employed, it is possible to convert \geq 84% of the incident photonic mode energy into the fundamental SPP mode [67] (consistent with other geometries [71]), which then propagates and gets concentrated at the nanoscale end of the taper without ever being cut off [10].

The concept of a robust 3D tapered structure forms the basis of the reproducible near-field campanile probes (Fig. 1(a)). The campanile geometry in this work consists of two symmetric linearly tapered Au cladding plates enclosing a SiO₂ core. Using nanofabrication techniques like focused ion beam (FIB) milling, metal deposition and, potentially, dielectric material deposition), this design can easily be integrated at the apex of a number of scan probe types including atomic force microscope (AFM) cantilevers or tapered optical fibers like those used in conventional aperture-based NSOM [9]. The campanile schematic shown in Fig. 1(a) is located at the end of a fiber probe, with a \sim 3-4µm opening at the MIM backside designed to match the core region of a chemically-etched optical fiber taper. As with the dimple lens [70], the campanile design can take advantage of thin-film growth/deposition capabilities to effectively define a nanoscale gap size smaller than what is reproducibly achievable using other nanofabrication techniques. While the gap size D_0 and width W_0 (see Fig. 1(a)) mainly determine the final spot size and field enhancement of the focusing point, the separation of the two metal plates Di will determine the efficiency of energy coupling from the photonic mode to the SPP mode, and the taper angle θ will determine the SPP transfer efficiency toward the end of the final aperture gap. For a linearly tapered two-dimensional (2D) MIM structure, the optimal taper angle is around $20^{\circ}-40^{\circ}$ [68], over which range the transfer efficiency shows only minor changes. For simplicity, we have used $\theta = 30^{\circ}$ in our simulations.

Simulations of electromagnetic properties of the campanile tips were performed using the finite element method (FEM) based on the commercial software COMSOL Multiphysics 4.2. Details of the simulations can be found in the SI of reference [9]. In short, the frequencydependent relative permittivity of gold $\mathcal{E}_{Au}(\omega) = \mathcal{E}_2(\omega) = \mathcal{E}_r - i \mathcal{E}_i$ was taken from Palik [72] and the refractive index of the SiO_2 layer was set as n = 1.5. For simplicity, plane wave excitation with an electric field component $E_v = 1$ V/m was sent into the simulation regime by scattering boundary conditions from the backside opening of the campanile structure (based on the similarity between the plane wave and the fundamental HE_{11} mode dominant in an optical fiber [73]). Since the 3D simulation of a full-sized structure placed prohibitive demands on the memory of our computing system, we performed 3D simulations of a number of smaller structure sizes to confirm that scaling trends held, then conservatively extrapolated to the length scales of real devices. The "small" simulations were essentially simulations of the end of a real-sized tip, taking care to capture the position on the structure where photonicto-plasmonic mode conversion occurs. Structural parameters in the simulations, unless defined otherwise, were: d = 50 nm, $\theta = 30^{\circ}$, $W_0 = 20 \text{ nm}$, $L_1 = 200 \text{ nm}$, $W_1 = 200 \text{ nm}$, $D_0 = 10^{\circ}$ 10 nm, $D_i = 200 \text{ nm}$ (Fig. 1(a)).

Calculated electric field distributions and enhancements are shown in Fig. 1(b). The highly localized field near the gap has an enhancement comparable to that from a bowtie or dipolar optical antenna with the same sized gap (gap = 10 nm) [37]. For comparison with other tip geometries given below, we use the convergent enhancement value at the gap center when appropriate (a few meshing layers away from the Au), where spurious unphysical field values from edge singularities in the simulation tend to be smoothed out. Simulations of structures with both sharp corners near the gap [9] and rounded corners (Fig. 1(b); 4 nm radii of curvature) were performed. The difference in the enhancement in those two cases is below

8%. Because of this modest difference, we use sharp corners in the following simulations of the campanile tip to reduce the simulation time. Also, the field polarization is aligned predominantly along the y axis near the gap, as expected.

As mentioned above, conical adiabatically tapered (CAT) tips offer field localization capabilities over a broad spectral bandwidth, as well as extremely large field enhancements when operated in tip-(metal) substrate gap mode, with the potential for nearly-backgroundfree excitation. In order to directly compare the campanile probes with these geometries, we have run simulations of both a CAT tip and a CAT tip in gap mode. For these, we modeled a 15 µm long Au CAT Au probe with a 20 nm radius of curvature and a cone semi angle of 15 degrees, similar to experiment [46]. The SPP wave was excited by defining a point magnetic current source at the base of the probe (this can also be thought of as assuming a 100% coupling efficiency of propagating light to the surface plasmons for the CAT tips). Figure 2(a), 2(b) shows the simulated distribution of |E| near the apex of a CAT tip in vacuum, while Fig. 2(c), 2(d) shows the calculated |E| for a tip located 2 nm above a Au substrate (both at λ = 667 nm). We see that the |E| enhancement at a point 1 nm from the tip apex is almost an order of magnitude larger for the tip-substrate gap mode. In addition, the broadband nature of the adiabatic taper can be seen in Fig. 3 (dark yellow curve, purple curve and black curves), where the enhancement values of a CAT probe in both normal and tip-substrate gap modes have been plotted for wavelengths spanning 500 - 1000 nm. Note that at wavelengths longer than ~ 650 nm, the spectral response is essentially flat, with the enhancement remaining large and nearly constant. As with any plasmonic system, the spectral response ultimately depends on the material-specific properties of the metal and surrounding material. Here, inter-band transitions in Au cause the enhancement to fall off at shorter wavelengths.



Fig. 2. Cross-sections of the electric field distribution surrounding a CAT tip in vacuum are shown in (a-b). For the simulations, plasmonic current sources are placed directly in the tip shaft. The field distribution cross-sections for a CAT tip in tip-substrate gap mode are shown in (c-d). In this case, the fields in the gap mode are much larger and more localized ($\lambda = 667$ nm).

To assess the relative merits of the campanile geometry, we simulated campanile probes with a 2 nm gap and 10 nm gap, a 20 nm radius CAT probe with a 2 nm tip-substrate separation, as well as an ultrasharp 2 nm radius CAT probe in vaccum. We note that reproducible growth of a 2 nm-thick dielectric (or even thinner) is quite feasible with current growth/deposition techniques. On the other hand, the 2 nm radius-of-curvature metalized

CAT probe may only exist in theoretical calculations because of metal material properties such as the stress-limited finite grain size of noble plasmonic metals. Furthermore, maintaining an ultrasharp tip on a soft plasmonic metal probe during scanning can be problematic in real experiments. The results of this simulation are plotted in Fig. 3 (blue curve), where it is shown that the smallest physical feature of the probe structure (e.g. the gap size or the tip radius) predominantly determines the final optical confinement and enhancement of all the adiabatic compression probes [74]. Note that the campanile tip provides nearly the same enhancement, ultralocalized field concentration (i.e. - high spatial resolution for imaging and spectroscopy), and broadband response, but without operating in tip-substrate gap mode. In other words, by effectively putting the gap on the tip while still utilizing plasmonic adiabatic compression, the campanile probes significantly increase the general applicability of nano-optical investigations (e.g. - samples with thickness greater than \sim 2nm can now be studied) without sacrificing the benefits associated with the more-limited tip-substrate gap modality. As with all near-field probes, the campanile tips also have the benefit of probing only surface/interface material located within a few nm of the tip, eliminating most background spectroscopic signal not arising from the interface region of interest (i.e. - there is very little excitation of signal from the "bulk", or from the surrounding solution if the tip is immersed in liquid [75]. Also, the electric field polarization for the campanile probe is in the plane of the sample, which is complementary to the CAT tip polarization that is primarily oriented normal to the surface.



Fig. 3. Electric field |E| enhancement vs. wavelength for a CAT tip in tip-substrate gap mode 2 nm above a gold substrate (purple curve), a CAT tip with 2 nm radius in vacuum (dark yellow curve), a campanile tip with a 2 nm gap at the tapered apex (blue curve), a CAT tip in vacuum (black curve), and a campanile tip with a 10 nm gap (red curve).

Also, visible in Fig. 3 are a couple of small oscillations in the enhancement spectrum of the campanile tip in the 650 - 800 nm region. These "wiggles" in the spectrum result from weak geometric resonances in the design. As with the CAT tip, enhancement falls off at shorter wavelengths due to interband transitions in the Au. Though not discussed here, we expect the large enhancements to extend well into the infrared (IR) region based on Au material properties (and suitable choice of dielectric material). Metals other than Au (e.g. Ag or Al) can be used for extending the enhancement into the blue, or even ultraviolet (UV), region of the visible spectrum. For demanding applications such as heat-assisted magnetic recording that require a particularly robust field-concentrating structure, transparent conducting oxides can be used as the plasmonic material if operating near the visible is not required [76].

As mentioned above, completely background-free near-field excitation is a clear goal for nano-optical imaging and spectroscopy. While an ideal adiabatic taper will concentrate and

guide the SPP mode toward the campanile apex without scattering light out, in practice it is likely that some radiation will scatter from the edges (and edge roughness) of the taper and onto the sample before reaching the tip end. In addition, a small fraction of the photonic mode that is not converted fully to the SPP mode by the campanile probe will also partially leak out from the Au-uncovered sides. For these reasons, we refer to the campanile tips as being "nearly-background-free" rather than strictly "background free", though based on simulations and preliminary experiments, we expect the intensity of this excess scattered light on the sample to be very small relative to the ultra-enhanced fields at the apex.

When considering that one will often operate in a mode where signal is collected back through the gap of the campanile tip, the total collected background from the sample arising from the edge-scattered light is expected to be insignificant, and so far has been below the noise floor in our experiments [9]. More extensive simulations (and hyperspectral imaging experiments) investigating this potential source of background are currently under way.

With regard to roughness, another potential advantage of the campanile geometry over the CAT tip is that it is less susceptible to surface roughness at the metal-dielectric interfaces of the waveguides, and thus to losses and other effects related to surface roughness along the tapered waveguide. This is because the optically-relevant surfaces of the campanile tip are formed by depositing the metal on a smooth dielectric, while the waveguiding metal-air surface of the CAT tips are often formed by evaporation or etching techniques (though advances based on template stripping have recently been demonstrated) [77].

In cylindrical coordinates, the equivalent of the MIM waveguide is a coaxial waveguide, which also supports a fundamental mode that propagates without cut-off no matter how thin the dielectric layer (see [41] and references therein). Therefore, a tapered coaxial waveguide will also have the benefits of the campanile tip when excited with radially polarized light. In this case, the localized, enhanced spot will be z-polarized and its size will be determined by the radius of curvature of the apex of the central pin. In passing, we note that it may be tempting to design a campanile-type tip with metal layers on all four sides of campanile structure in order to create a polarization-insensitive structure, as in the case of cross optical antennas [78–80]. However, even with the four sides of the waveguide being electrically isolated from one another, all modes supported by this geometry will be cut off when the thickness of the dielectric is tapered below a certain value; i.e. – it behaves very similarly to a conventional aperture-based NSOM probe.

Besides efficiently concentrating light to nanoscale dimensions, reciprocity would imply that the campanile probe also efficiently collects emission [81], and simulations show that this is indeed the case. To understand this, we simulated a larger scale campanile structure probe with an electric dipole located near the middle of the nano-gap (Fig. 4). The dipole was positioned 2 nm away from the campanile apex in the z direction and oscillated along the y direction. In this simulation, the campanile structure sits near the end of a tapered optical fiber (20 degree taper; Nufern 780-HP fiber $n_{core} = 1.4597$, $n_{cladding} = 1.4535$), which has a 4.4 μm core size. The backside aperture of the campanile structure is 1.5 µm by 1.5 µm in size (Fig. 4) and is located at a position on the fiber where the fiber taper reaches a diameter of 3 μ m. Both the total emitted power from the dipole and the power in the fiber at the position where the tapered optical fiber reaches its full core size were calculated. The latter represents an estimate of how efficiently the SPPs in the campanile back-couple to the photonic mode in the optical fiber. Figure 4(b) shows that the total power emitted by the dipole is largely enhanced (more than 1000 times) compared with the same dipole in vacuum. These numbers are similar for a CAT probes either in tip-substrate gap mode or with ultrasharp (~ 2 nm) tip radii. In addition, more than 90% of that total emitted power is directed into the campanile MIM waveguide (Fig. 4(a), 4(c)). This efficient emission collection can be attributed to the large optical density of states at the campanile probe apex and the enhanced spontaneous emission near the Au cavity. Also notable is that > 50% of the power reaches the fiber core in

the campanile probe (Fig. 4(a), 4(c)), with metal losses and radiation accounting for the bulk of the lost power.

Finally, we emphasize the breadth of optical characterization techniques that are possible at the nanoscale using optical transformer-type probes such as the campanile tip, which combines wide bandwidth with maximum field enhancement and resolution. This tip geometry provides near-optimal excitation and collection properties for nano-Raman and nano-IR/FTIR hyperspectral imaging and also enables measurements such as white-light nano-ellipsometry/interferometric mapping of dielectic functions, nonlinear optical experiments that involve multiple optical frequencies (such as sum-frequency and secondharmonic generation), coherent anti-Stokes and stimulated Raman spectroscopy, as well as other ultrafast pump-probe investigations of local dynamics [82].



Fig. 4. FEM simulations of a campanile structure located on a tapered optical fiber, with an emitting electric dipole oriented along the y direction, centered on the gap and located in the z-axis 2 nm away from the tip apex. Values of $W_i = D_i = 1500$ nm, Au film thickness = 300 nm, $D_o = 10$ nm were used here. (a) The yz-section of the steady-state electric field amplitude near the end of the probe, with the dipole emission wavelength $\lambda = 713$ nm. (b) Enhancement of the dipole's total emitted power (black curve) and the emitted power reaching the optical fiber core (red curve) vs. wavelength, relative to the dipole in vacuum. (c) The percentage of emitted power that reaches the optical fiber core (red curve) vs. wavelength.

In conclusion, we have compared the "campanile" probe paradigm with other nano-optical probe geometries. This type of hybrid photonic-plasmonic structure geometry effectively marries the beneficial properties of photonic waveguides, plasmonic waveguides, and optical antennas. We used FEM to simulate conventional aperture-based probes, traditional apertureless NSOM tips and the state-of-the-art adiabatic-compression-type probes, examining their nano-optical properties relative to those of the campanile structure. More specifically, beyond insights from the circuit theory of metal-optics [11], understanding of the relative strengths and weaknesses of each NSOM probe geometry served as the guideline for the design of the campanile tips, resulting in their superior field coupling, spectral bandwidth, enhancement and resolution capabilities. We expect these types of probes to have a broad impact as they enable a general approach towards manipulating light and the investigating light-matter interactions at the nanoscale.

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