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A gold-nanotip optical fiber for plasmon-enhanced near-field detection

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A wet-chemical etching and mechanical cleaving technique is used to fabricate gold nanotips attached to tapered optical fibers. Localized surface plasmon resonances (tunable from 500 to 850 nm by varying the tip dimensions) are excited at the tip, and the signal is transmitted via the fiber to an optical analyzer, making the device a plasmon-enhanced near-field probe. A simple cavity model is used to explain the resonances observed in numerical simulations. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4813115>]

Localized surface plasmon resonances (LSPRs) are collective oscillations of the surface electrons that appear at sharp features (corners or edges) in metallic nanostructures when excited by an electromagnetic (EM) field.^{1–5} Their optical properties are determined both by the permittivities of the metal and the surrounding dielectric and by the morphology of the nanostructure.⁶ LSPRs are accompanied by strong local EM field enhancement, making them useful in areas such as surface-enhanced Raman spectroscopy⁷ (SERS), nonlinear optics,⁸ photovoltaics,^{9,10} and biophotonic sensing.^{11,12}

Metal nanotips in particular are of considerable interest because the nanoscale field localization at the tip^{13–16} allows the optical resolution of sub-10 nm features by rastering the surface. Such probes are used in tip-enhanced Raman spectroscopy^{17,18} (TERS) and scattering near-field optical microscopy^{19,20} (s-SNOM), the most recent application being in gate-tunable graphene plasmons.^{21,22} Metal nanotips are typically fabricated by electrochemical etching²³ or by focused ion beam (FIB) milling²⁴ resulting in intensity enhancements of 10^6 for TERS.

In this letter we introduce a fiber-coupled plasmon-enhanced near-field optical probe based on a metallic nanotip attached to the end of a tapered multimode (MM) fiber. The nanotips have apex radii below 10 nm and show strong LSPRs. Part of the light in the LSPRs is scattered into the taper where it is collected by the MM fiber and can be easily delivered to, e.g., a detector or a spectrometer. The technique used to fabricate these nanoprobe is straightforward and does not require any sophisticated nanostructuring or deposition equipment. Numerical simulations of the metallic nanotips show a blue-shift of the LSPR for broader tips and multiple LSPRs for longer tips. To explain these properties, we introduce a plasmonic cavity model in which it is assumed that a surface plasmon polariton (SPP) propagates back and forth along the tip,¹³ forming a standing wave pattern and a defined cavity mode. The model allows the number and positions of the LSPRs to be calculated for various

tip geometries. Experimentally we can fabricate nanoprobe custom-designed to support a single LSPR at wavelengths from the visible to the near-infrared.

The fabrication process involved a combination of etching, mechanical cleaving, and splicing (Fig. 1(a)). First a gold-filled silica capillary (125 μm outer diameter, 1 μm gold

FIG. 1. (a) Sketch of the fabrication procedure (from left to right): etching with 40% HF acid, scratching, cleaving, and splicing. The horizontal blue dashed lines indicate characteristic positions of the fabrication process. All images are not to scale. (b) SEMs of two different metal tips. The left-hand image shows a top view (the background is air), the center image shows a tilted view from the front (light grey is gold, dark grey is silica), and the right-hand image is a close-up of the black rectangle. The white scale bars show 10, 0.5, and 0.1 μm (from left to right).

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FIG. 2. Schematic of the device (not to scale). Upper: sketch of the front end of the nanoprobe. The grey color depicts silica and the yellow color gold. The vertical blue dashed lines indicate the geometrical dimensions of the probe. Lower: the optical signal (red color), i.e., the collected light from the tip, travels from the tapered region (bottom left) towards the end of the MM fiber (top right) inside the fiber core.

wire diameter), fabricated in a previous step in a fiber drawing tower,²⁵ was etched using a wet chemical process. This etching procedure is known as *Turner's method*²⁶ and involves dipping the capillary into a solution of 40% hydrofluoric (HF) acid (left-hand image in Fig. 1(a)). We terminated the etching process after ~ 50 min (at standard ambient conditions), at which point the part of constant outer diameter was reduced to $20\ \mu\text{m}$. Surface tension at the silica-HF interface results in the formation of a meniscus, leading to a gradient in the etching rate (slower at the top, faster at the bottom) and taper formation. The etched capillary was then

scored close to the taper (center image in Fig. 1(a)) either manually or, for more precision, using FIB milling. Upon subjecting the score to axial tension the capillary could be cleaved manually. Since gold is a ductile material, the wire undergoes plastic deformation during cleaving, forming a sharp metallic nanotip.²⁷ The fused silica, in contrast, always cleaves flat. Fig. 1(b) shows scanning electron micrographs (SEMs) of two nanotips made using this approach (left-hand image: FIB scratching; center: manual scratching). For all the samples investigated the wire protruded several μm out of the silica, forming a tip. The smallest apex radii achieved by this method was below 10 nm. Many of the samples, while otherwise smooth, showed a pronounced sharp edge at the base of the actual tip (see close-up, right-hand image in Fig. 1(b)), some 100 nm before the apex. In a final step, the capillary was cleaved ~ 1 cm from the taper and spliced to a MM fiber (GeO₂-doped SiO₂ core, $100\ \mu\text{m}$ in diameter, right-hand image in Fig 1(a)).

A sketch of a typical probe is shown in Fig. 2. The gold nanotip is attached to a wire that protrudes several μm from the tapered end-face. The sharp edge at the base acts as a reflector, leading to the formation of LSPRs that radiate into free space. Part of the emitted light is collected by the tapered silica capillary incorporating the gold wire. The taper channels the light to the far end by total internal reflection at the silica-air interface, where it is collected by the spliced MM fiber. The fiber is connected to optical detectors used to analyze the signal.

Using a numerical Maxwell solver (Comsol finite element, FE), we investigated the scattering of a plane wave at an isolated nanotip in air (Fig. 3(a)). Since the sharp edge at the base of the nanotip (see Fig. 2) acts as a strong reflector for propagating surface plasmons, we consider only the section between the tip and the sharp edge, neglecting the rest of the nanowire. We used the parameters for silver instead of

FIG. 3. (a) An incident plane-wave scatters at a silver nanotip (the grey semi-ellipse shows the axial cross-section with base diameter $2a$ and tip length b) and excites a LSPR. The curved green strip at the apex shows the surface charge density σ (not to scale). (b) The FE-computed field enhancement factors 5 nm above the tip apex for base radii of 25 nm (red curve) and 50 nm (blue curve), keeping b constant at 200 nm. (c) The field enhancement factors for $b = 150$ nm (green curve) and 300 nm (orange curve), keeping a constant at 25 nm. The vertical dashed lines and circles indicate the resonance positions obtained from the cavity model (see Fig. 4). (d) Normalized intensity of the scattered field in a plane passing through the tip axis for the $q = 1$ (left) and $q = 2$ (right) LSPRs of the green curve from sub-figure (c). The white dashed lines indicate the silver-air boundary and the arrows highlight the intensity maxima.

gold in order to avoid the effects of interband transitions in the visible, which would obscure the physics of the cavity model described below. The tip is modelled as a semi-ellipsoid with minor and major axes a and b , the dispersive dielectric function being taken from tabulated literature.²⁸ The polarization of the electric field is parallel to the major axis of the tip (red double-headed arrow in Fig. 3(a)). The simulation area of $2.5 \times 2.5 \mu\text{m}$ was terminated by perfectly matched layers. The circular symmetry of the structure was used to reduce computation time, and the consistency of the results was checked by comparing with analytic Mie-scattering at a silver nanosphere.⁶ We investigated different tip geometries and found LSPRs from the visible to the near infrared. When the length of the tip is kept constant ($b = 200 \text{ nm}$), a single LSPR is found that shifts towards shorter wavelengths as the base diameter $2a$ is increased (red and blue curves in Fig. 3(b)). At resonance, the field amplitude at the tip is ~ 100 times stronger than in the incident plane wave. When the diameter is kept constant ($a = 25 \text{ nm}$), more and more LSPRs appear as the overall length of the tip increases (green and orange curves in Fig. 3(c)).

These properties can be explained by a cavity model, in which we assume that the LSPRs are formed by a SPP propagating to and fro between the apex and the base of the tip ellipsoid (Fig. 4(a)).^{13,29} Because the attenuation length L_p of the SPP is much greater than the physical length of the tip ($L_p/b \sim 30$ at 633 nm , calculated at the base), a clear resonance can form. Besides energy dissipation in the metal, an additional loss channel is partial reflection at the base, which results in a reduction in the quality factor of the resonator. If λ is the vacuum wavelength of the driving field, the resonance condition is

$$q\lambda = 2 \int_{\text{base}}^{\text{apex}} n(z) dz, \quad (1)$$

where q is the mode order of the LSPR. The local modal index n is determined by the real part of the (complex) root of the eigenvalue equation³⁰

$$\frac{\varepsilon_M}{\varepsilon_D} = -\frac{\kappa_M I_0(k_0 \rho \kappa_M) \times K_0(k_0 \rho \kappa_D)}{\kappa_D I_1(k_0 \rho \kappa_M) \times K_1(k_0 \rho \kappa_D)}, \quad (2)$$

where ε_M and ε_D are the permittivities of the metal and the dielectric, $\kappa_M = (n^2 - \varepsilon_M)^{1/2}$ and $\kappa_D = (n^2 - \varepsilon_D)^{1/2}$ are the SPP parameters, $I_{0,1}$ and $K_{0,1}$ are modified Bessel functions of first and second kind, $k_0 = 2\pi/\lambda$ is the vacuum wave vector and $\rho = \rho(z)$ the radius at distance z from the tip. Fig. 4(b) plots the modal index as a function of z at 633 nm for an ellipsoid with $a = 50 \text{ nm}$ and $b = 200 \text{ nm}$ (same parameters as for the blue curve in Fig. 3(b)), showing that it increases considerably close to the tip. For more elongated tips the integral in Eq. (1) has a larger value, resulting in a red shift of the fundamental LSPR ($q = 1$) and the appearance of higher order LSPRs ($q \geq 2$). In Figs. 3(b) and 3(c), the resonant wavelengths obtained from Eq. (1) are shown as vertical dashed lines where the integration is terminated at a cut-off radius of 1 nm . This radius was chosen because at sub-nanometer dimensions the local metal permittivity is

FIG. 4. (a) Plasmonic cavity model: a fundamental SPP is reflected at the top end (base) of the ellipsoid (blue color) and forms a cavity mode. The black double-headed arrows indicate the counter-propagating SPPs. The normalized doughnut-shaped intensity distributions (not to scale) of the SPP are shown at three positions of the resonator: base, center, and apex. (b) Modal index of the SPP at 633 nm dependent on the position along the tip (blue curve). The grey shaded area indicates an axial cross section and the horizontal black dashed line shows the symmetry axis of the ellipsoid. The geometric parameters are the same as for the blue curve in Fig. 3(b).

determined by quantum mechanical effects³¹ that are neglected here. The model reproduces the number of resonances obtained from FE simulations and approximately gives the resonance positions, showing that the LSPRs form as described in this simple model.

Fig. 3(d) shows the intensity distribution of the scattered field in a plane passing through the tip axis for the $q = 1$ (left-hand image) and $q = 2$ (right-hand image) LSPRs of an ellipsoid with $a = 25 \text{ nm}$ and $b = 150 \text{ nm}$ (same parameters as for the green curve in Fig. 3(c)). Note that the field peaks only at the tip apex for the fundamental LSPR; for the first higher order mode an additional field maximum appears, as expected. In the $q = 2$ case the intensity inside the metal is higher, which is the result of the fact that the electric field parallel to (and continuous across) the silver-air interface is higher.

The optical characteristics of the device were measured by probing the evanescent optical near-field at the base of a prism (set-up sketched in Fig. 5(a)). Broadband, p- or s-polarized light from a supercontinuum (SC) source was weakly focused by a lens (L1, focal length 75 mm , NA 0.17) on to the base of the prism (Thorlabs GGG coupling prism, $n = 1.9$ at 633 nm). Total internal reflection created an evanescent field that penetrated a few 100 nm into air, the reflected beam was blocked by a beam dump (BD). Using piezo-controlled stages (PI Nanocube P-611.3 S), the nanoprobe was brought into close proximity with the prism base, allowing the nanotip to interact with the evanescent field.

For p-polarized light a LSPR was excited at the tip, and could be directly observed in an inverted optical microscope. For the example presented here (top image in Fig. 5(a)), a diffraction-limited green spot is seen at the end of the wire

FIG. 5. (a) Experimental set-up, not to scale. The top image is an optical micrograph, the image to the right is a $5\times$ magnified view of the LSPR at the tip apex. The vertical white dashed line indicates the prism-air interface. The yellow dashed lines highlight the boundaries of the silica taper, the gold wire (see orange arrows) is protruding out several μm . The white scale bar shows $20\mu\text{m}$. (b) Normalized spectra of three different tips. (d) Spectra from tip (2) for p- and s-polarized input light.

(close-up is shown in the top right-hand image). Part of the scattered light is collected by the taper (highlighted by the yellow dashed lines) and transmitted via the MM fiber to an optical spectrometer (Ocean Optics QE65 Pro).

Since the spectral position of the LSPRs depends strongly on the morphology, each nanotip must be characterized in advance of any application. Three example spectra (normalized to their maximum value) are shown in Fig. 5(b), the green curve (1) corresponding to the sample showing the green spot in Fig. 5(a). For this nanotip, the fundamental LSPR is centered at $\sim 580\text{ nm}$ with a full width at half maximum (FWHM) of $\sim 90\text{ nm}$. The other two nanotips have LSPRs at 675 and 760 nm . The LSPRs were much more strongly excited by p-polarized light (see Fig. 5(c) for tip (2)), as expected. The small residual peak seen for s-polarization results from a slight oblique position of the nanotip with respect to the normal of the prism-air interface. Note that in all measurements the spectral transmission function of the entire device is included.

In summary, a combination of wet chemical etching, mechanical cleaving, and optical splicing has allowed us to produce a type of plasmon-enhanced near-field fiber probe, in which light from a LSPR on a gold nanotip is collected by a fiber taper and is guided via a MM fiber to an optical spectrometer. LSPRs, tunable from 500 to 850 nm varying the tip design, can be excited by placing the tip in an evanescent field. A simple cavity model allows the number and approximate wavelengths of each resonance to be predicted. This nanotip-fiber device is likely to find applications in TERS, near-field microscopy and sophisticated experiments on light-matter interactions at the nanoscale.

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