Design of plasmonic probe tips to control light on the nanoscale for imaging and spectroscopy with ultrahigh spatial and temporal resolution

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Introduction: The characterization of the chemical composition of heterogeneous catalysts, organic nanocomposites, or semiconductor heterostructures requires spectroscopic access to these highly inhomogeneous materials with spatial resolution down to nanometer length scales for, e.g., advanced solar energy and fuel cell applications. The extension of conventional optical spectroscopy to the nanoscale through new near-field based approaches (scattering near-field microscopy) as in-part developed by our group [1-5] has proven this capability. However, challenges associated with efficient nanoscale light localization, precise control and probe sensitivity with respect to polarization, and high signal background levels that require different modulation schemes have so far prevented these techniques from routine applications.

In this proposal, we suggest *two new methods for high-sensitivity optical probing at the nanoscale*. The first involves the nanofocusing of optical fields using tapered metal tips. This provides a nanoconfined light source at the apex enabling low-background (high signal to noise ratio) optical probing with nanometer spatial resolution. The second relies on the nanoengineering of the optical antenna properties of a tapered probe tip to optically interrogate vector-resolved electric near-fields of nanoparticles and nanoscale optical devices in three dimensions with nanometer spatial resolution allowing for measurement of the current density and electrical impedance distribution in optical antennas.

Part I: A nanoconfined plasmonic light source for imaging and spectroscopy with ultrahigh spatial and temporal resolution

Background: The precise control of optical fields on the nanoscale is highly desired for new developments in nanoscale optical microscopy and surface enhanced spectroscopy. In this respect, surface plasmon polaritons (SPP) in metallic nanostructures offer the most versatile optical excitation [6]. They allow for surface-bound electromagnetic energy transport and focusing.

In our group we take advantage of the plasmonic local field enhancement and confinement at the apex of tapered metallic scanning probe tips. This allows for the technique of apertureless or scattering-type near-field microscopy (*s*-SNOM) [1-5] that reaches beyond what can be achieved by conventional near-field microscopy in terms of nanometer spatial resolution [3], single molecule sensitivity [4], and accessible spectral range from UV to THz [1, 5]. However, the large scattering background and finite degree of field localization as a result of the direct illumination of the tip-sample gap makes signal detection in general, and the implementation of time-resolved spectroscopies in particular, difficult.

Objective: The goal of this project is the design of tips with high capture cross section and efficient nanometer field confinement at the apex. Periodic structures on metallic surfaces allow for the resonant excitations of SPPs via grating coupling [6]. The subsequent propagation gives rise to an enhanced and confined field at the apex (for underlying physical mechanism see below) as shown by us previously [7]. Focused ion beam milling (FIB) will be used to write grating coupler, Bragg reflector, and spectral and phase pulse shaper into the tip shaft. In addition, the tip apex itself will be nanomachined for desired plasmon resonances.

This allows for optimizing (i) the SPP excitation process, (ii) the plasmon propagation, and (iii) the efficiency of the transformation into a localized excitation for maximum brilliance at the apex region as determined by apex

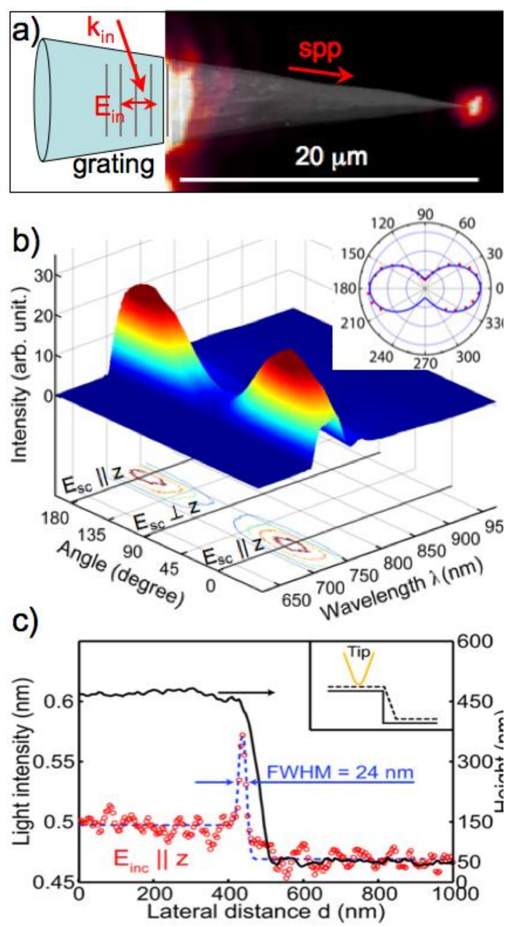

Fig. 1 Grating coupling of surface plasmons onto metallic tip-shaft, its subsequent nonradiative propagation to tip apex, and reemission as a truly nanoconfined light source (a). Spectrally resolved polarization anisotropy of tip radiation corre-sponding to a Rayleigh emitter (b). Surface scan using Si sample step edge indicating a sub-10 nm emitter size after tip deconvolution (c).

angle, radius, and structural plasmon resonance of the apex itself, ultimately enabling tuning of both the spectral and ultrafast characteristics of the field.

The successful design of plasmonic scanning probe tips with these tailored optical properties will allow us to perform nearly background-free *s*-SNOM with ultrahigh temporal and spatial resolution. Performing near-field Raman spectroscopy without direct far-field illumination at the apex, we expect to circumvent problems arising from far-field background signal and sample bleaching. Measuring the frequency dependent group velocity dispersion delay in the taper using interferometric measurements will allow us to implement pulse shaping to minimize the pulse duration at the tip apex. We expect this to allow for the first experiments with simultaneous *nanometer spatial and femtosecond temporal resolution* providing access to the dynamics of mesoscopic phenomena at dimensions of the electron or phonon scattering length scales (for, e.g., molecular nano-composites, transition metal oxides).

Extension to the mid-infrared: We will furthermore pursue the extension of grating coupling for nanofocusing on tapered metallic tips into the mid-infrared spectral region to enhance vibrational IR-s-SNOM [3]. For their characterization and *s*-SNOM implementation we will use both a table-top tunable IR laser source from difference frequency generation of 10 fs Ti:S pulses and the IR beamline 1.4.4 at the Advanced Light Source at the Lawrence Berkeley Laboratory (beamline proposal accepted, ranked top 2 out of 14 submissions). In collaboration with Viktor Podolskiy at Oregon State University (joint ONAMI grant), theoretical designs of mid-IR tips will be implemented and tested for optimal IR light coupling and propagation. Nanometer IR light concentration will enable local field-enhanced IR vibrational spectroscopy. IR grating coupling experiments could also pave the way to *IR plasmonics*, with waveguides exhibiting millimeter, rather than micrometer, propagation distances compared to the visible spectral range.

Previous related work at EMSL: The work outlined for this project is in part an extension of the recently completed EMSL proposal 26701 and the currently active general use proposal 38203. In two years with 11 2-3 day visits to EMSL, we have laid the groundwork for nanoemitter optical probe experiments, investigating correlations between tip design and SPP coupling efficiency, SPP mode propagation, and emission size [8]. After optimizing the tip design with regard to grating depth, width, smoothness, SPP propagation length, and cone angle, we can now consistently produce tips with strong SPP excitation and localized nanometer scale emission at the apex.

This work answered long-standing questions regarding the proposed mechanism of adiabatic SPP propagation [9, 10] and focusing on a metallic taper especially under the symmetry breaking excitation conditions with the SPP modes representing a multimode excitation. From the polarization of the apex emitted light we confirm that only the m=0 fundamental radially symmetric TM mode nanofocuses at the apex prior to breakdown of the adiabatic condition (Fig. 1b). In scattering experiments on a sharp Si step edge, an emitter size of only *~10 nm* was found, comparable to the tip apex radius (see Fig. 1c) with nanoconfinement and focusing efficiency ~100 times higher than what can be achieved by far-field focusing. These results suggest many exciting new applications for these tips including extreme spatial resolution imaging, data recording, attosecond XUV generation, and antenna-based molecular sensing. Figure 2 shows preliminary spectra measured using grating-coupled excitation for tip-enhanced Raman scattering (TERS) on a monolayer of the dye IR-125 (Exciton, Inc.). The onset of signal at distances of <5 nm is related to the near-field nature of the Raman excitation and a direct result of the high degree of spatial confinement achieved. The high degree of background signal suppression is evident, with negligible signal for distances > 5 nm.

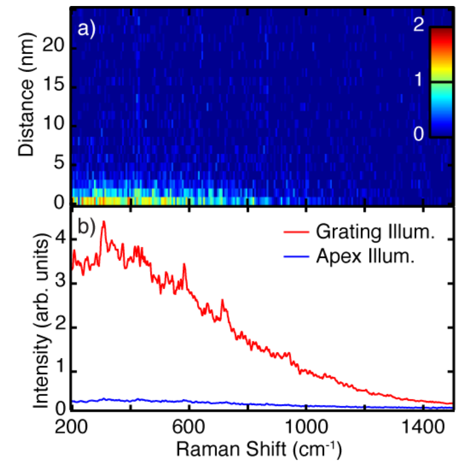

Fig. 2. Preliminary TERS data using grating-coupled plasmon nanofocusing. a) spectra acquired with the tip approaching a monolayer of the dye IR-125. b) com-parison of grating-coupled and direct apex illumination showing the improved focusing efficiency for this geometry.

Proposed work at PNNL: Conical Au and Ag wire tips will be prepared by electrochemical etching. The grating coupler and tip apex region will then be nanomachined to the desired shape according to theoretical designs with a precision down to 10 nm, using the dual-beam focused ion beam/scanning electron microscope (FIB/SEM) at the EMSL user facility. The tips will then be used for tip-enhanced linear (e.g. Raman), nonlinear (e.g., SHG, CARS), and ultrafast *s*-SNOM experiments for the optical probing of, e.g., organic semiconductors, semiconductor heterostructure nanocrystals, and magnetoelectric multiferroic nanocrystals as supported by grants from NSF (Career), DoE (SISGR), ONR (ONAMI), and ACS (PRF).

Part II: Optical antenna characterization with a nano-optical vector network analyzer

Background: As indicated above, *s*-SNOM allows for highly spatially resolved probing of chemical and optical properties of materials. To achieve optimum performance of emerging nanophotonic and plasmonic devices for spectroscopy, molecular sensors, and nanocircuits, it is critical to understand the correlation of device structural and material properties with desired optical properties as characterized by the electrical source current distribution within the devices, or equivalently, through the associated electric and magnetic fields around the devices. However the nanoscale measurement of these optical antenna device parameters has not yet been possible, even though it is needed for the design of high efficiency, impedance-matched optical antennas and antenna-coupled sensors.

Objective: The goal of this project is to extend the capabilities of *s*-SNOM probe tips [5, 11] by designing and fabricating tips with optical nano-probe antennas located at the apex in order to controllably scatter specific electric field vector components in the near-field for the characterization of optical antennas and antenna-coupled plasmonic waveguides and sensors. Complete knowledge of the electric near-field gathered in this way, with amplitude, phase, and orientation information in three dimensions, will allow for the calculation of both the local magnetic field and internal current density in the excited structures with nanometer resolution, providing a new design tool for nano-optical systems with extremely high sensitivity, small footprint, and high optical conversion efficiency.

Proposed work at PNNL: The FIB/SEM uniquely enables the nanoengineering of probe tips for optical near-field investigations. At EMSL, we will mill the apex of a silicon AFM probe tip using FIB milling in preparation for subsequent optical antenna fabrication at the apex. Using nanoscale electron beam assisted chemical vapor deposition (nano-CVD) within the FIB chamber, we will then deposit platinum by way of the built-in gas injection system to fabricate a suitable near-field scatterer in the form of an optical antenna at the apex. Further milling of the platinum will allow us to define our antenna type, including linear Hertzian dipole antennas, broadband spiral antennas, or highly directional Yagi-Uda antennas. Through a collaboration with Glenn Boreman at the University of Central Florida CREOL, who specializes in infrared antenna fabrication, the probe tips will then be used to measure the electromagnetic characteristics of infrared antenna-coupled molecular sensors and infrared thermal nanosensors with high sensitivity and enhanced optical capture cross section. This work is supported by NSF (IGERT), DoE (STTRII) and ONR (ONAMI) grants.

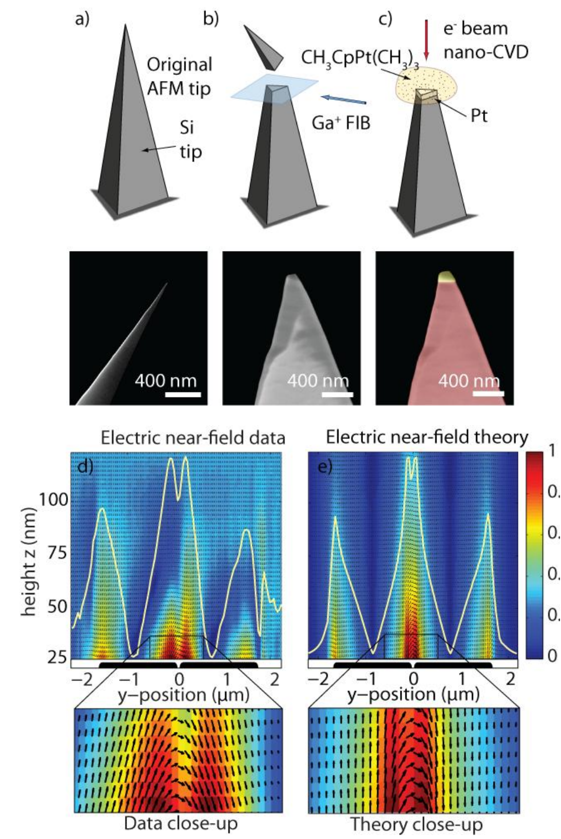

Fig. 3. Vector imaging with a FIB modified tip. (a-c) tip modification process via FIB/SEM. The modified tip enables the complete measurement of the near-field of, e.g., an optical antenna (black bars) (d) in good comparison to theory (e) with amplitude (color scale) and phase (arrow orientation) resolution. The solid line shows the normalized field magnitude at a height of 25 nm.

Preliminary results: Preliminary work in this regard has been done at the EMSL user facility under proposal 26701. Using the technique described above, we have created a probe antenna on the apex of a tip. The specific electric-field vector scattering capabilities of the modified tip have enabled, for the first time, the complete measurement of the vector field of a Au linear dipole infrared optical antenna on a Si substrate using *s*-SNOM (see Figs. 3d and 3e). Through Hallen's integral equation and Faraday's Law respectively, it is then possible to derive the current density *within* the optical antenna and the associated magnetic field [12] improving upon previous attempts. Further EMSL support will allow us to optimize the probe antenna parameters including tuning, scattering bandwidth, and directionality through the investigation of new antenna designs.

Requested resources: As the continual design, fabrication, and optimization process for new types of tips and tip-coupled antennas is time intensive, for these two projects, approximately 20 hours per 2 months of FIB/SEM time is requested for tip fabrication. Access to the clean room during this time is also requested for sample preparation and analysis using the thermal evaporator and profilometer.

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Addendum 2. CVs

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Developing and use of linear and nonlinear optical scanning probe techniques for imaging with nanometer spatial and femtosecond temporal resolution: Studying light-matter interaction on the nanoscale, engineering plasmonic nanostructures for optical nanofocusing, vector-field imaging of IR optical antennas and devices, investigating electron and vibrational dynamics of metal nano-particles and molecular nano-composites, and phase behavior and domain formation in transition metal oxides (metal-to-insulator transitions, multiferroics).

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SELECTED PUBLICATIONS

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Addendum 3: EMSL Resources

Resource Requested	**# of Samples**	**Units Requested**	**Period of Use**	**Project Team Expertise**	**EMSL Support Requested**
FIB/SEM	5 tips	120	20 hrs/month x 6 months	Grad student will mill tips	Staff help to train student
Clean Room	5 tips	10	Intermittent use for sample prep	Grad student will perform sample prep	None needed