Rationally Designed Nanosensing Substrates for Chemical and Biodetection

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The focus of this Nanoscale Interdisciplinary Research Team is to develop a comprehensive fundamental understanding of nanostructure-enhanced chemical detection (Fig. 1). Chemical sensing has evolved into a mature technology where breakthroughs are required for further

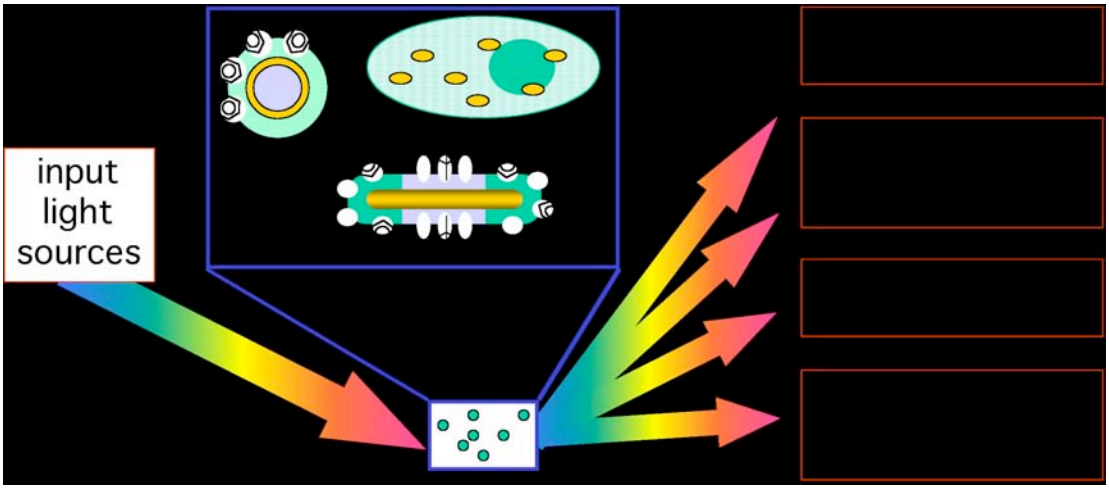

Figure 1. Schematic of chemical detection approach. Nanostructures designed for specific surface-enhanced spectroscopies all provide fingerprinting information for remote detection of chemicals (upper left and bottom) and may be selectively bound to biological agents (upper right) for optical identification.

significant advances in detection sensitivity. Recent advances in surface-enhanced spectroscopies have shown that enormous detection enhancements are possible when molecules are adsorbed onto metallic nanostructures, where the plasmon resonant properties of the nanostructure greatly intensify the optical frequency field at the nanostructure surface. Although surface-enhanced spectroscopies have been studied both experimentally and theoretically for over 25 years, it is only now, with advances in precise nanofabrication methods and powerful theoretical tools, that a systematic and quantitative characterization of these effects at the nanoscale is possible. Developing methods to predict, control and optimize these electromagnetic enhancements and understanding their influence on surface-enhanced spectroscopies is the primary purpose of this proposed project. The research goals of this team are:

- to design, construct and optimize nanostructure-based substrates for ultrasensitive detection of molecules based on Surface Plasmon Resonance Spectroscopy, Surface Enhanced Raman Spectroscopy, Fluorescence Spectroscopy, and Surface Enhanced Infrared Spectroscopy.

- to develop a comprehensive fundamental understanding of nanostructure enhanced chemical detection by accurately modeling the substrate, the molecule, and the near field at the substrate-molecule interface, based on full quantum-mechanical methods and

computational electrodynamics. This will lead to the development of nanoscale design rules for the optimization of the specific spectroscopies under development, and will permit the optimization of nanoscale detection systems for chemical specificity.

- to apply this foundational understanding to the chemical detection of small molecules, functional groups characteristic of chemical, biological and explosive agents, to proteins, and ultimately to micron-sized, protein-coated objects, mimicking the transmembrane proteins of bacteria or the protein coat of bacterial spores.

The specific nanostructure geometries which will be the focus of this work are:

(a) ***individual nanoshells,*** where the molecule of interest is positioned on the surface or a controlled distance from the surface using either a silica-based or peptide-based spacer. The distance dependence and the dependence of the plasmon resonance relative to the relevant energy states of the molecule will be systematically varied for each spectroscopy of interest, as appropriate.

(b) ***individual nanorods***, either fabricated using wet chemistry or nanopatterning methods, where the molecule of interest is positioned on or near the surface and the transverse or longitudinal plasmons will be selectively excited. The nanorod plasmons will be systematically varied as is suitable for each spectroscopy of interest.

(c) nanocavities, formed by ordered or patterned aggregates of two or more tunable plasmon resonant nanostructures, shown here as two nanoshells. In these cases the frequency-distinct dimer plasmon can selectively be excited and can probe molecules deposited within the nanocavity.

(d) nanoarrays, formed by various nanopatterning methods, support plasmons and can be used as rationally designed substrates for plasmon-enhanced spectroscopies. These arrays can also be used as molecular "landing pads" for assembling nanorod or nanoshell structures in controlled geometries on surfaces.

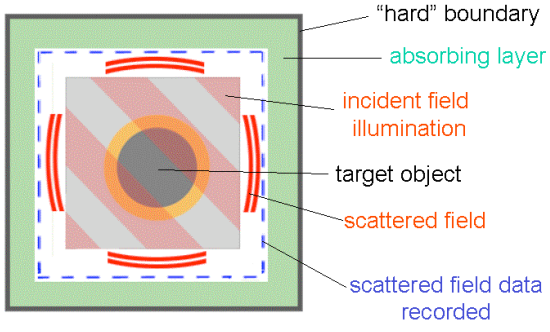

Figure 2. FDTD simulation geometry for plasmon-enhanced spectroscopies. Our code allows the user to specify the size, shape, and material of the target object(s) and the nature of the incident excitation, allowing for arbitrary waveforms, incident directions and amplitudes.

The theoretical analysis and design tools developed in the course of this project will be used to develop a comprehensive understanding of the local electromagnetic environment of plasmonic nanostructures. The principal theoretical approach that will be used is the Finite-Difference Time-Domain (FDTD) discrete method (Fig 2). This method involves the discretization of Maxwell's equation on a spatial grid and the propagation of the local electric and magnetic fields in real time. Our plans are:

- to develop and optimize our FDTD code for the calculation of the electromagnetic fields in the proposed plasmonic structures fabricated in this project;
- to utilize our code as a predictive design tool to guide all aspects of nanostructure fabrication and molecular placement for plasmon-enhanced spectroscopies.