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Surface-Enhanced Raman Scattering Optical Fibers as Chemical Sensors

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Introduction & Background

In this project, a surface-enhanced Raman scattering (SERS) based optical fiber sensor is designed to monitor pH in real time. SERS spectra of reporter molecules adsorbed on the fiber are used to deliver information on the chemical composition of the environment.

Raman Spectroscopy. Raman spectroscopy is a vibrational spectroscopy that results from an inelastic energy exchange between an incident photon and matter (Figure 1). The energies of inelastically scattered photons can be used to measure characteristic vibrational frequencies of molecules (ν_{vib}). While researchers have long recognized the potential analytical applications of Raman spectroscopy, the small Raman cross section (~10^{28} - 10^{-30} cm^2) has limited sensitivity.

Surface-Enhanced Raman Scattering (SERS). In 1977, two independent groups[1,2] reported the SERS phenomenon that was first observed by Fleischmann and coworkers in 1974.[3] For molecules adsorbed on roughened metal surfaces, the Raman scattering cross section (σ_{vex}) is enhanced as much as 15 orders of magnitude, enabling detection and identification of single molecules.[4-7] Both electromagnetic enhancement (EME) and chemical enhancement (CE) mechanisms have been proposed to explain the SERS phenomenon (Figure 2).

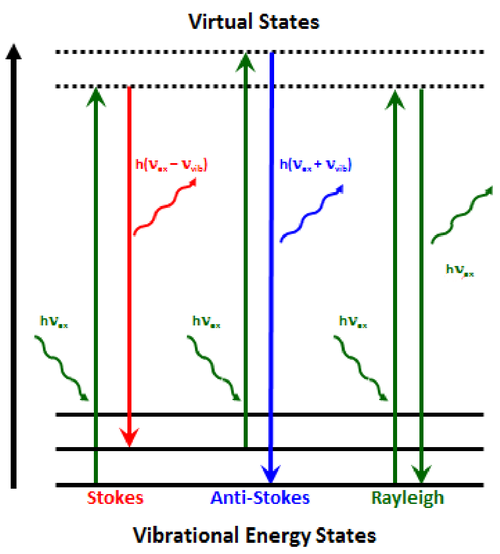

Figure 1. ***Raman Scattering.*** An incident photon (green) excites a ground state molecule to a virtual excited state. Upon relaxation, the molecule can scatter a photon of longer (red) or shorter (blue) wavelength.

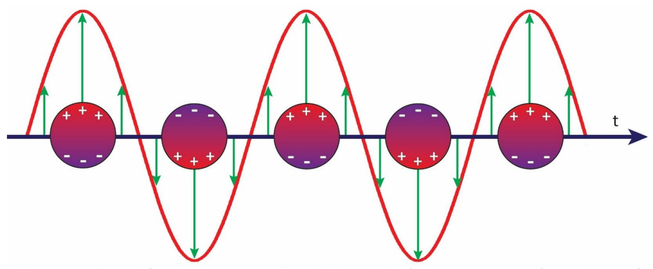

Figure 2. ***Electromagnetic SERS Enhancement by Metal Nanoparticles.*** When the incident light strikes the surface, localized surface plasmons are excited.

Methods

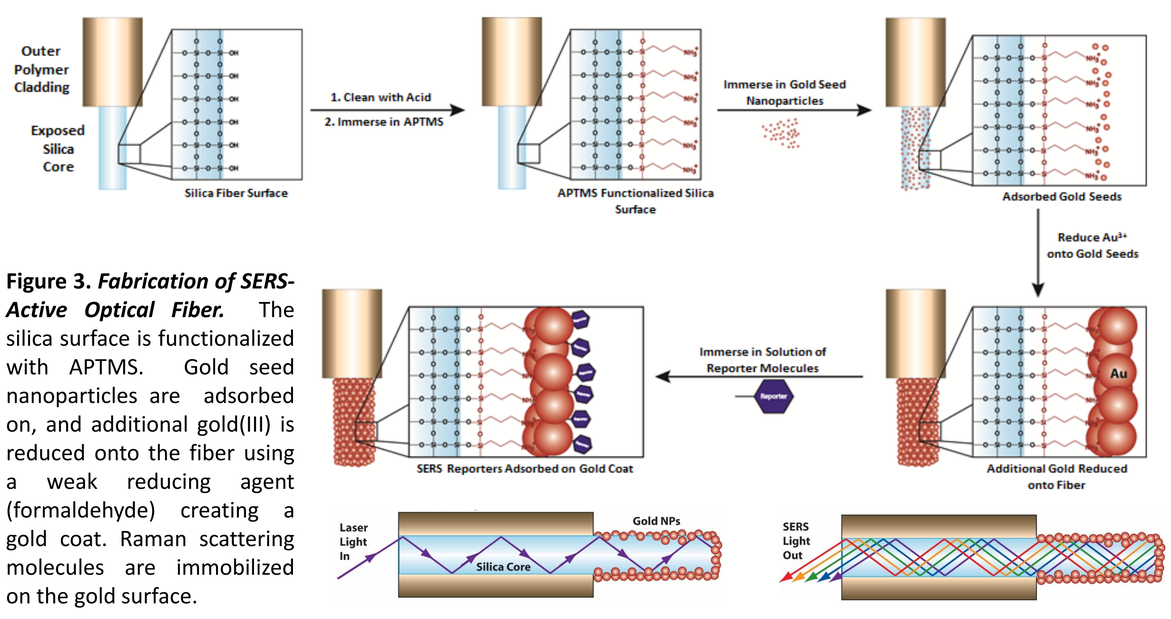

Figure 3. ***Fabrication of SERS-Active Optical Fiber.*** The silica surface is functionalized with APTMS. Gold seed nanoparticles are adsorbed on, and additional gold(III) is reduced onto the fiber using a weak reducing agent (formaldehyde) creating a gold coat. Raman scattering molecules are immobilized on the gold surface.

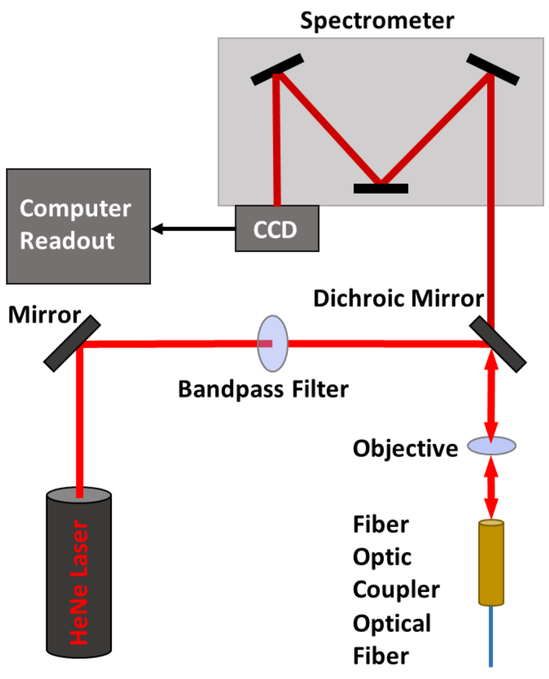

Figure 4. ***Spectrometer Setup for Collecting SERS Spectra.*** A 632.8 nm helium-neon laser is focused directly through the optical fiber to induce Raman scattering of reporter molecules adsorbed on the gold-coated tip. The resulting inelastically scattered photons travel back through the fiber and into the spectrometer. These hit a reflective grating, where they are turned onto a Czerny-Turner monochromator. A focusing mirror focuses the light onto the CCD (charge-coupled device). The charges accumulated on the camera are then translated into a spectrum on the computer.

Experimental Results

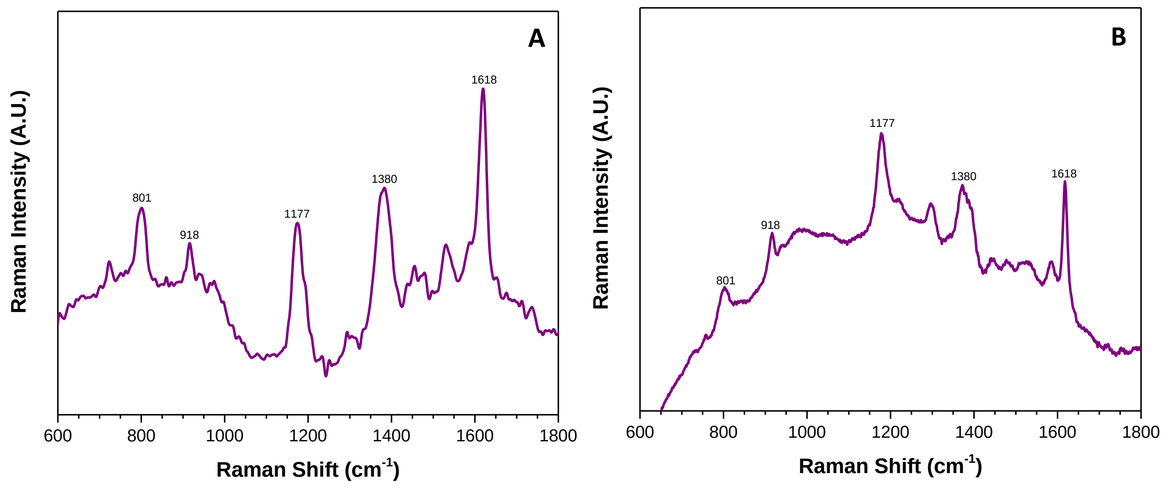

Figure 5. ***SERS Spectra of Crystal Violet Molecules Adsorbed on Gold-Coated Optical Fiber Sensor.*** **(A)** SERS spectrum of crystal violet (CV) acquired by focusing the excitation laser onto the exterior of the gold-coated tip and collecting the Raman scattered photons at 180° to the laser. **(B)** SERS spectrum of CV acquired by coupling the excitation laser into the optical fiber and collecting the backscattered Raman photons through the same fiber.

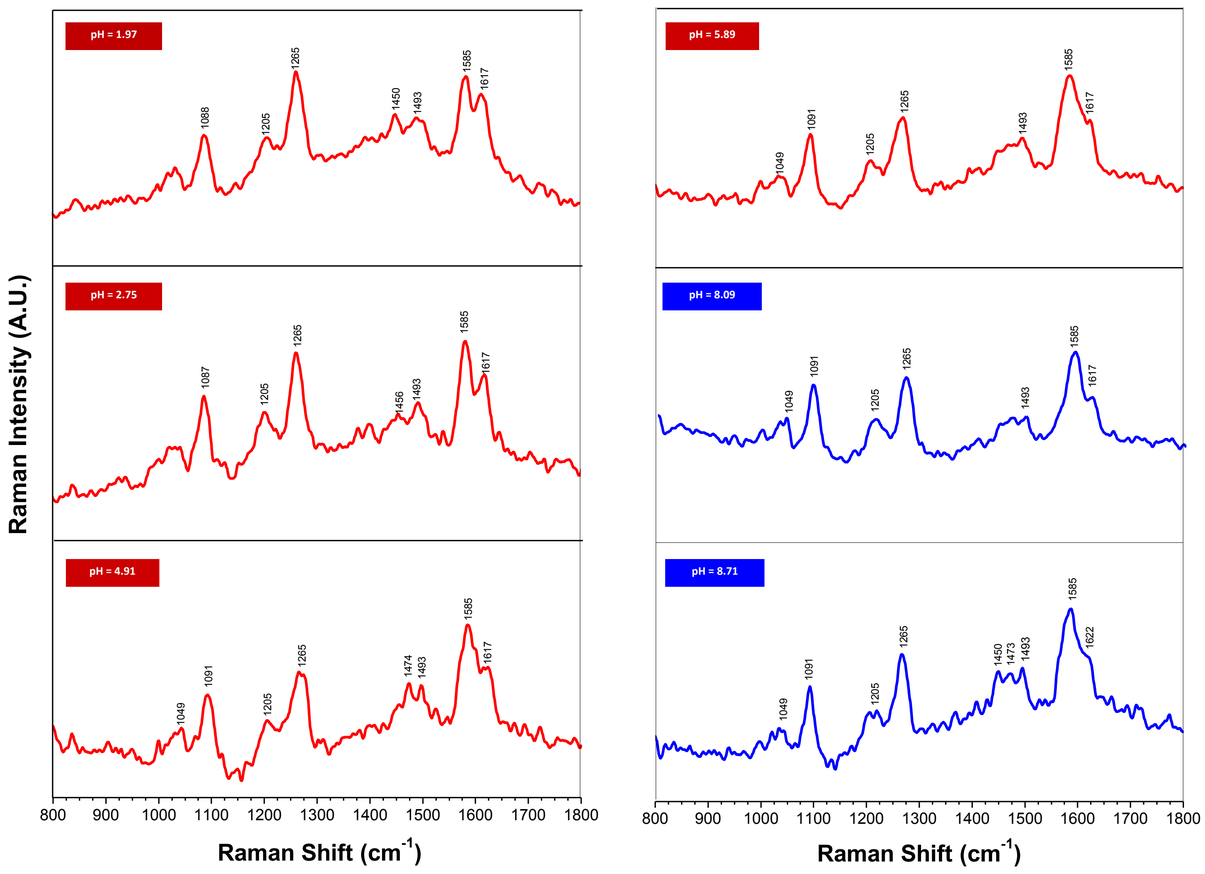

Figure 6. ***Far-Field SERS Spectra of 4-Mpy Adsorbed on Gold Coated Optical Fiber at Varied pH.*** One fiber was used to obtain all spectra using a far-field Raman spectrometer. The peak near 1610 cm^{-1} is pronounced at low pH. As pH increases the peak becomes less intense. In addition, the peak near 1585 cm^{-1} increases in intensity as pH increases. The ration of the intensities of these peaks can be used to quantify pH. λ_{ex}=633 nm, t_{int}=5 s.

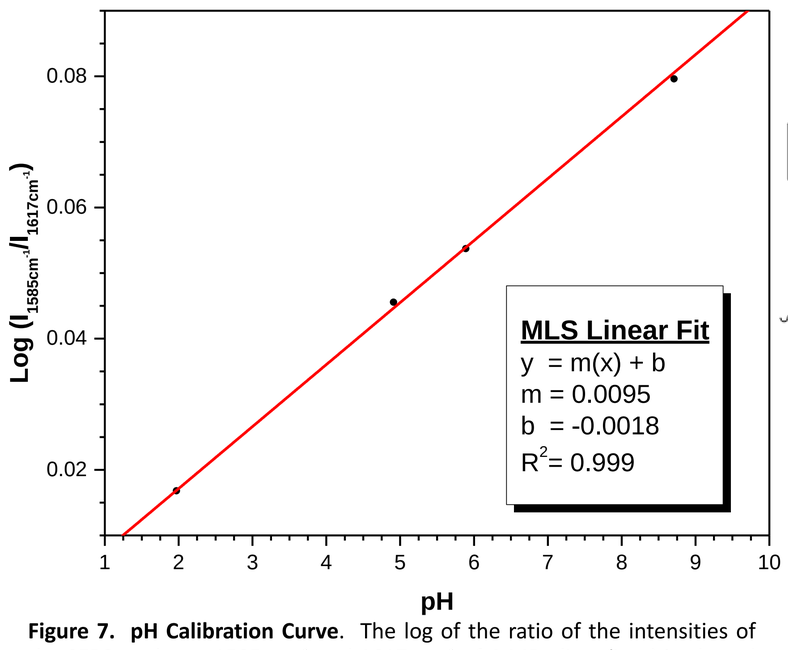

Figure 7. pH Calibration Curve. The log of the ratio of the intensities of the SERS peaks at 1585 cm^{-1} and 1617 cm^{-1} of 4-MPy (I_{1585}/I_{1617}) is plotted versus pH. The best fit line demonstrates the strong correlation between the log of the ratio of these peaks and pH.

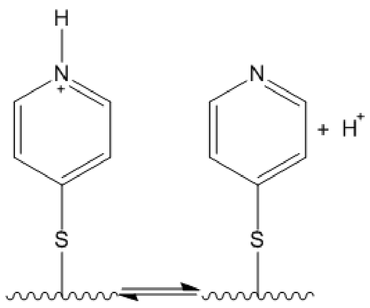

Figure 8. ***Deprotonation of 4-mercaptopyridine.*** At low pH, the aromatic amine of 4-mercaptopyridine (4-MPy) is protonated but loses its proton as the pH is increased.

Conclusions & Future Work

The self-assembled gold monolayer is grown on the surface of the optical fiber, and can be used to detect SERS of reporter molecules. 4-Mercaptopyridine (4-MPy) has been shown to be SERS active and its spectrum changes based on its protonation state. Therefore, 4-Mpy can be used to sense changes in pH. In our group, this has been shown by collecting spectra at varying pH by focusing laser light onto the gold coated fiber when 4-Mpy is adsorbed. Moving forward, the spectra will be obtained through the fiber sensor and used to monitor pH in real time.

References

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Acknowledgements

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