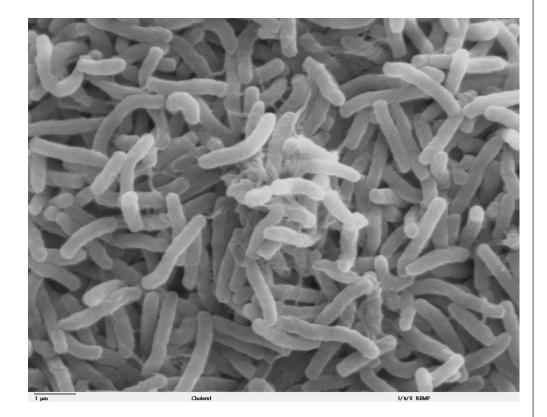
Preparing Metal Tips Suitable for Tip Enhanced Raman Spectroscopy

- Veronica Mota
- Ventura community college
- Environmental Science major
- Lab Mentor: Isaac Riisness
- Faculty Advisor: Mike Gordon
- Chemical Engineering Department
- Funding: CNSI Seed Fund

The Big Picture

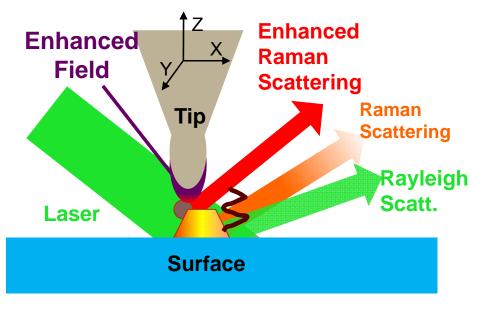
- Surface chemical imaging via Raman Spectroscopy.
- TERS; Physical properties and chemical properties of molecules as well.
- Applications; images of biomolecules and study of catalytic surfaces.



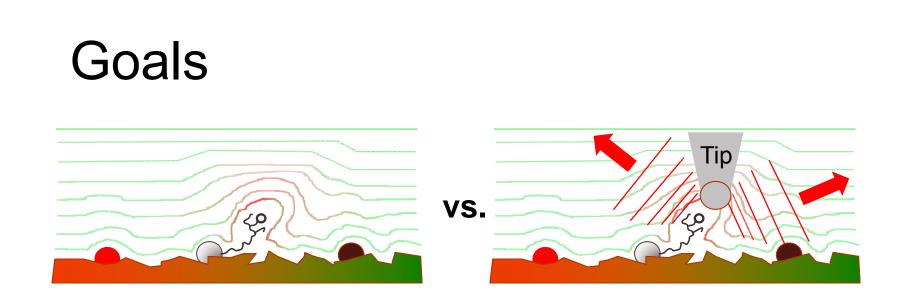
Picture of E.coli bacteria taken with SEM.

Tip Enhanced Raman Spectroscopy(TERS)

- Laser is directed at surface and metal tip.
- Molecule; two types of scattering occurs.
- Tip; laser light excites electrons.(plasmonic coupling)
- Enhanced Electromagnetic field is created.
- Only Gold and Silver can be used.



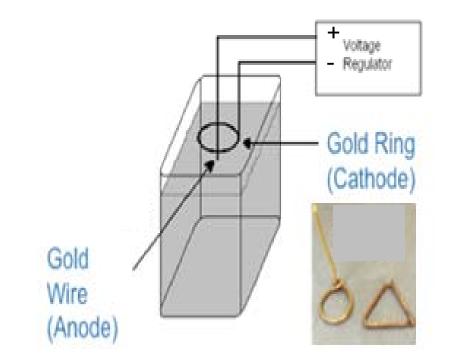
Tip enhanced Raman spectroscopy enhances Raman scattering.



Tip Enhancement Allows Sub-λ details to propagate

- Metal tip is the main reason for field enhancement.
- Quality of tips is of importance, the sharper the tip the better the enhancement.
- Preparation and Characterization of metal tips to be used in Tip-enhanced Raman Spectroscopy.

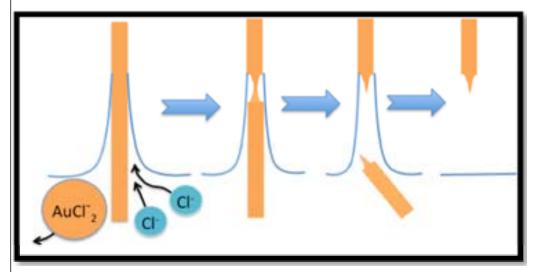
Electrochemical Etching Setup for Gold Tips





- Electrolyte composed of 1:1 HCI and Ethanol by volume.
- The gold ring and wire are suspended from hooks which are in turn connected to a voltage regulator.
- The anode is connected to the (+). The cathode is connected to the (-).

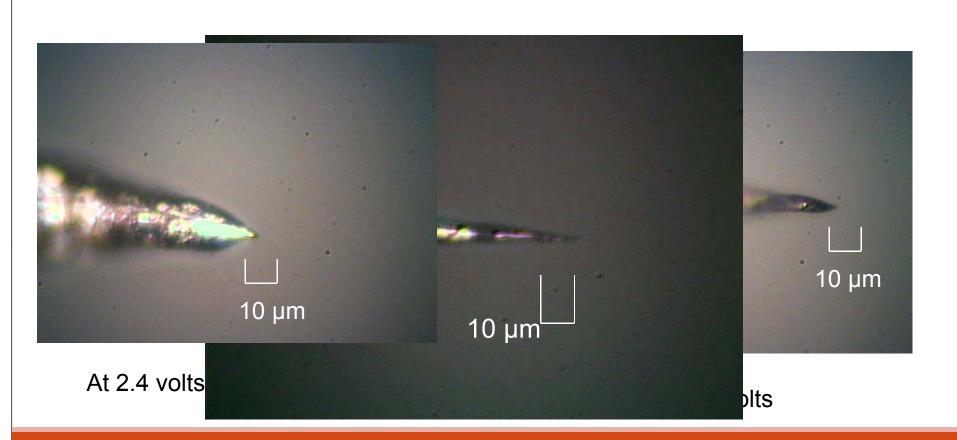
The Etching Process



Reactions Occurring:

 $\begin{aligned} AuCl_{4}^{-}+3e^{-} &\longleftrightarrow Au+4Cl^{-}, E_{0}=1.002V\\ AuCl_{2}^{-}+e^{-} &\Leftrightarrow Au+2Cl^{-}, E_{0}=1.154V\\ AuCl_{4}^{-}+2e^{-} &\Leftrightarrow AuCl_{2}^{-}+2Cl^{-}, E_{0}=0.926V \end{aligned}$

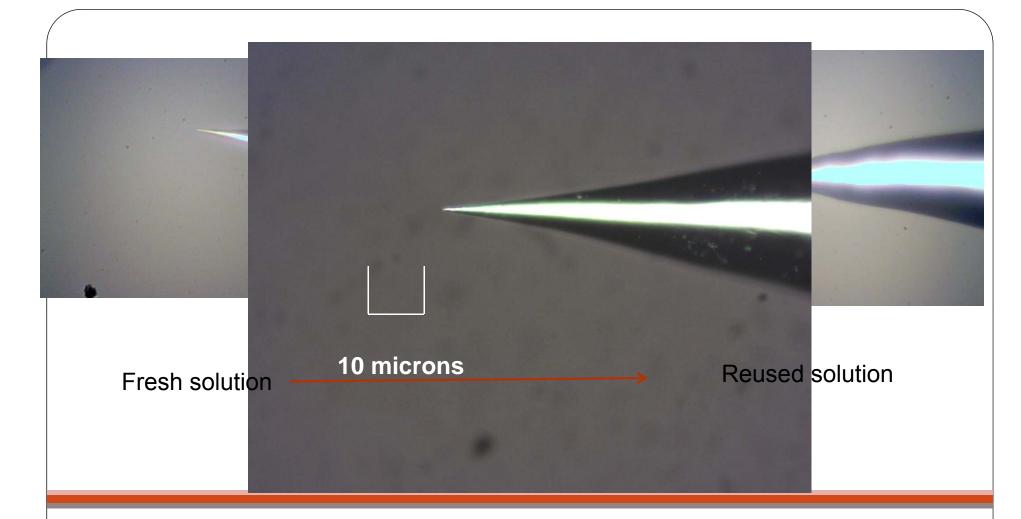
- Chloride ions react with the gold wire producing AuCl₂ in solution.
- The CI ions keep trying to react with the gold in the wire.
- Voltage regulator stops the etching process.



Gold tip etching

•Preferred voltage is 2.4-2.5v for .250 mm wire in HCI/Ethanol solution.

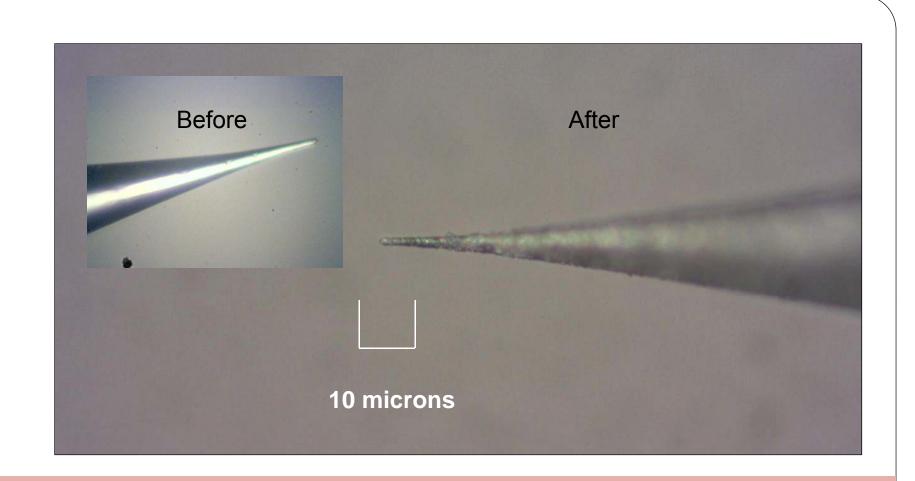
•After experimenting with new wire(0.04mm) realized smaller wire requires smaller voltage.



Tungsten Etching

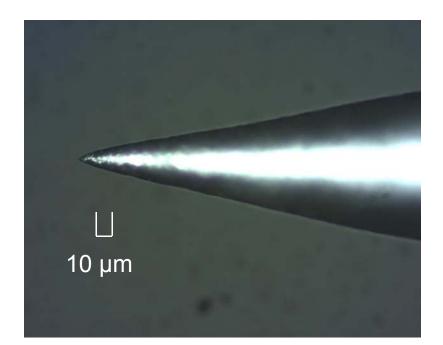
•Preferred voltage 7.5v in 3M KOH solution

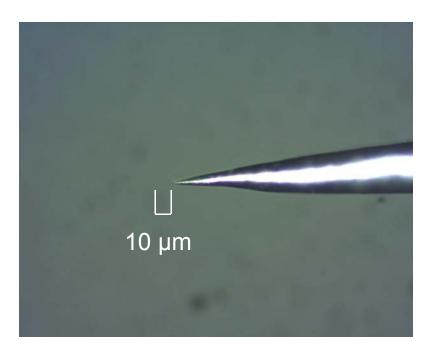
•Concluded tip quality becomes worse after subsequent reuse of solution.



Tungsten silver plating

- •Plating solution composed of AgNO₃, KI and H₂SO₄
- •Voltage of 3.0 v
- •Reaction time 20-30 seconds





First trial silver etching

New solution etching

Silver Etching

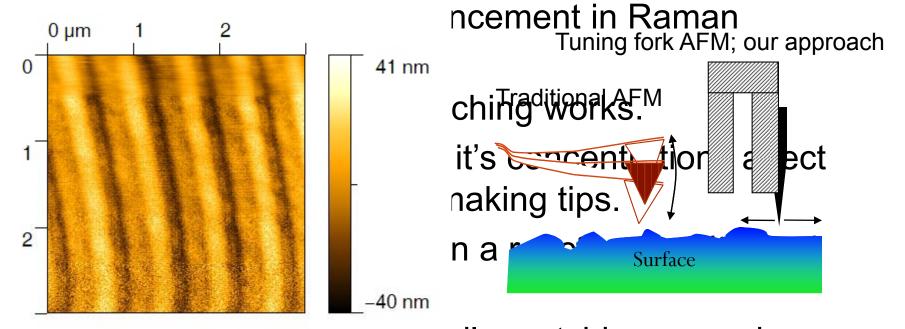
•First trial electrolyte: ethanol, ammonia, and Hydrogen peroxide, 20-24 v

- Resulted in dull tips
- •New Solution: Ammonia /Ethanol 5:1 by volume
- •Voltage; 10.5v

Summary

- Several different tips were made in different solutions and voltages.
- **Gold**; smaller wire requires smaller voltage.
- **Tungsten**; reuse of solution produces less fine tips over time.
- **Silver**; produced successful tips with ammonia ethanol electrolyte.

Achievements



- Achieved a succession silver etching procedure.
- Used tungsten tips in AFM (atomic force AFM scan with tungsten tip microscopy) calibration.

Future Plans

- Improving silver etching
- Using gold and/or silver for actual TERS
- Seeing if silver plating of Tungsten will in fact produce successful scans.

Acknowledgments

- UCSB
- INSET staff
- INSET group members for helpful feedback
- P.I Mike Gordon
- Mentor Isaac Riisness
- Entire Gordon Lab