Project # 81939

Hybrid Micro-Electro-Mechanical Systems (MEMS) for Highly Reliable and Selective Characterization of Tank Waste

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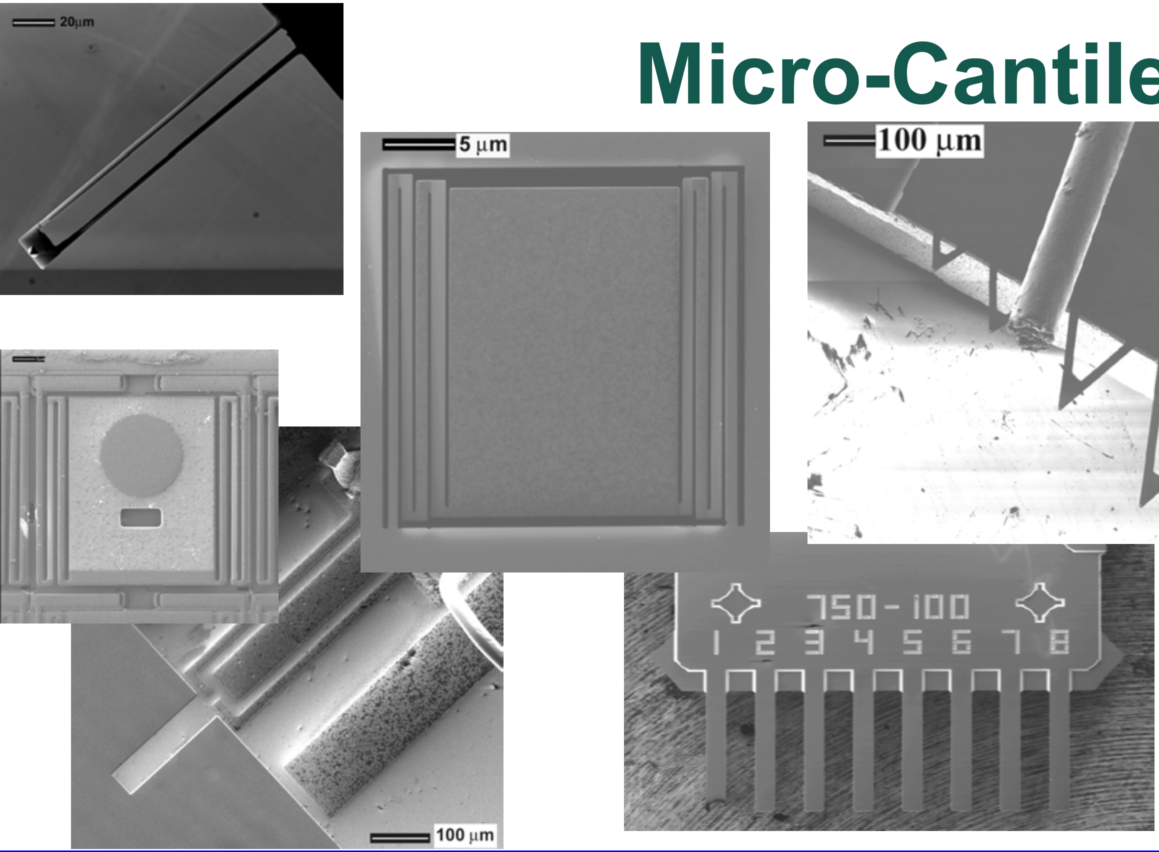
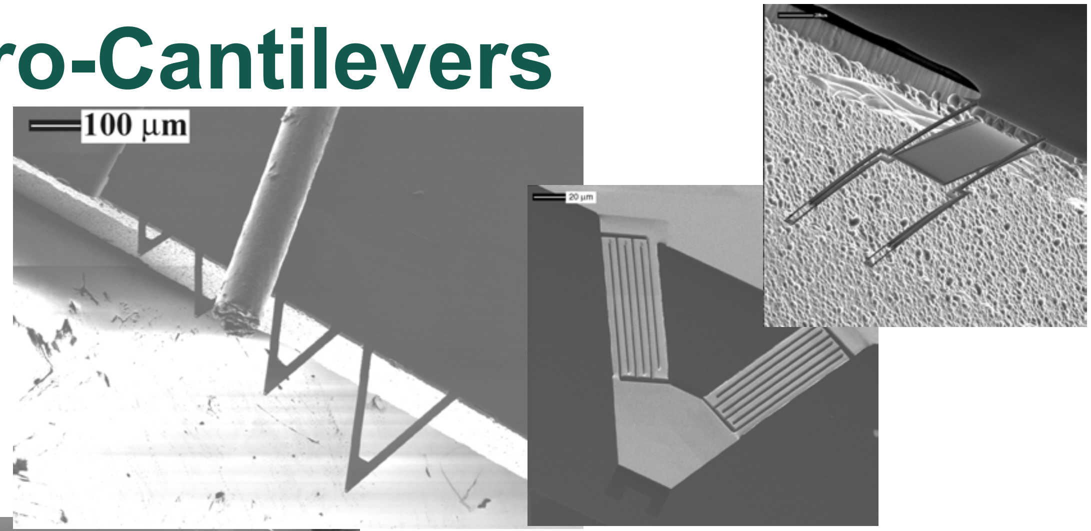
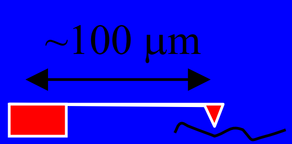
Micro-Cantilevers





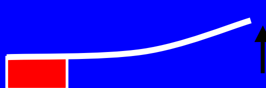
Length	**: 50- 500 µm**
Width	**: 10-100 µm**
Thickness	**: 0.1-4 µm**

Microfabricated cantilevers:



AFM probes

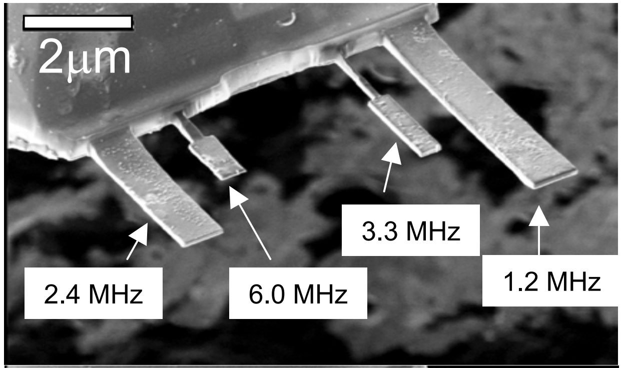
Mass-sensitive resonating devices

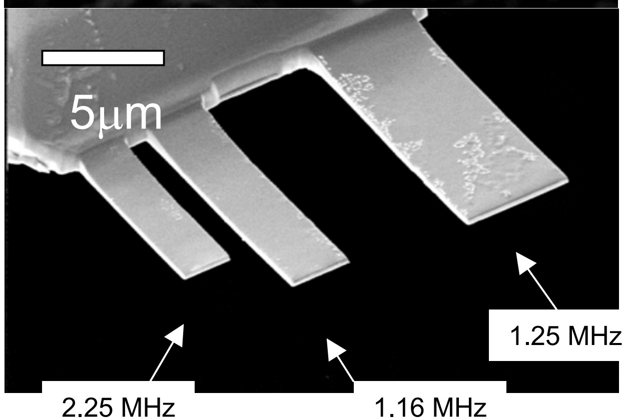


(static bending mode)

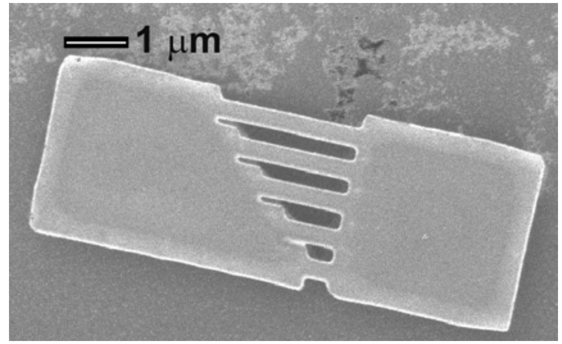
Very high surface-to-volume ratio ⇒ significant contribution of surface forces into a total energy

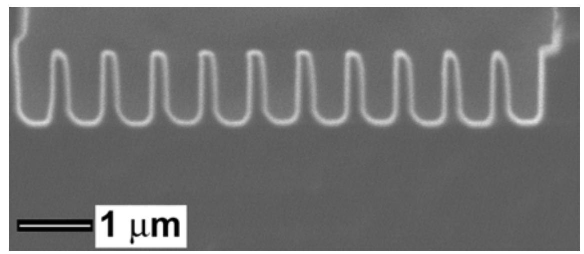
Micro/Nano Devices

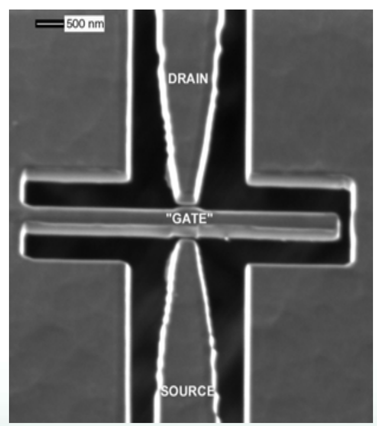


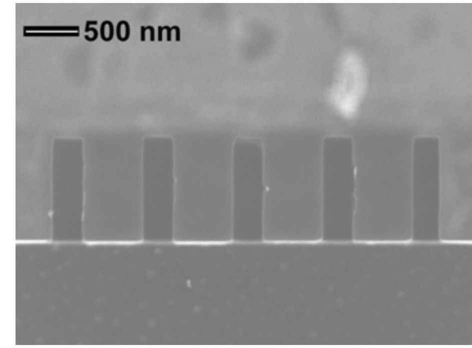


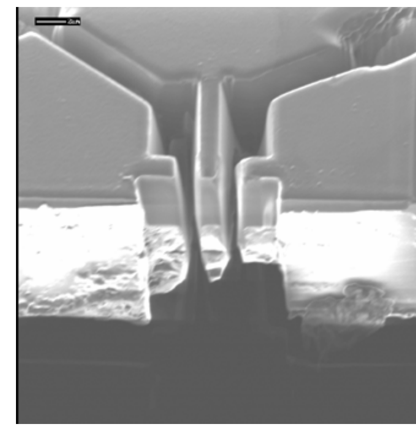
Length	**: 2 – 9 μm**
Width	**: 1 - 4 μm**
Thickness	**: 50 - 100 nm**







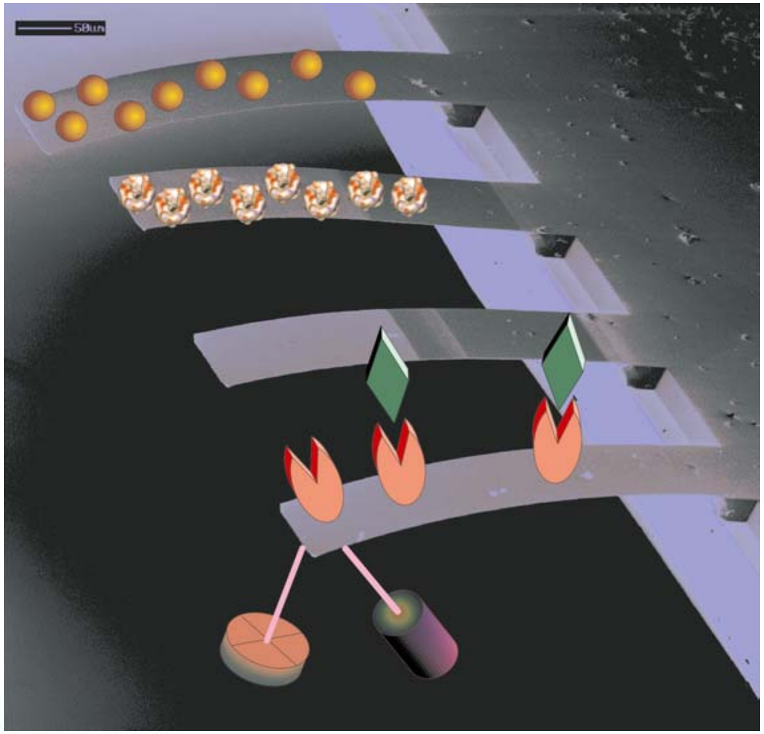




Length	**: 20-1000nm**
Width	**: 10-200 nm**
Thickness	**: 10-50 nm**

Objectives and Challenges

- Integrated chemical sensors (microfluidics & MEMS)
- Molecular recognition in sensing
- Transducers with enhanced response characteristics
- Hybrid sensors combining different sensing concepts to enhance performance
- Devices combining sensing & actuating functions (chemi-mechanical transistors)



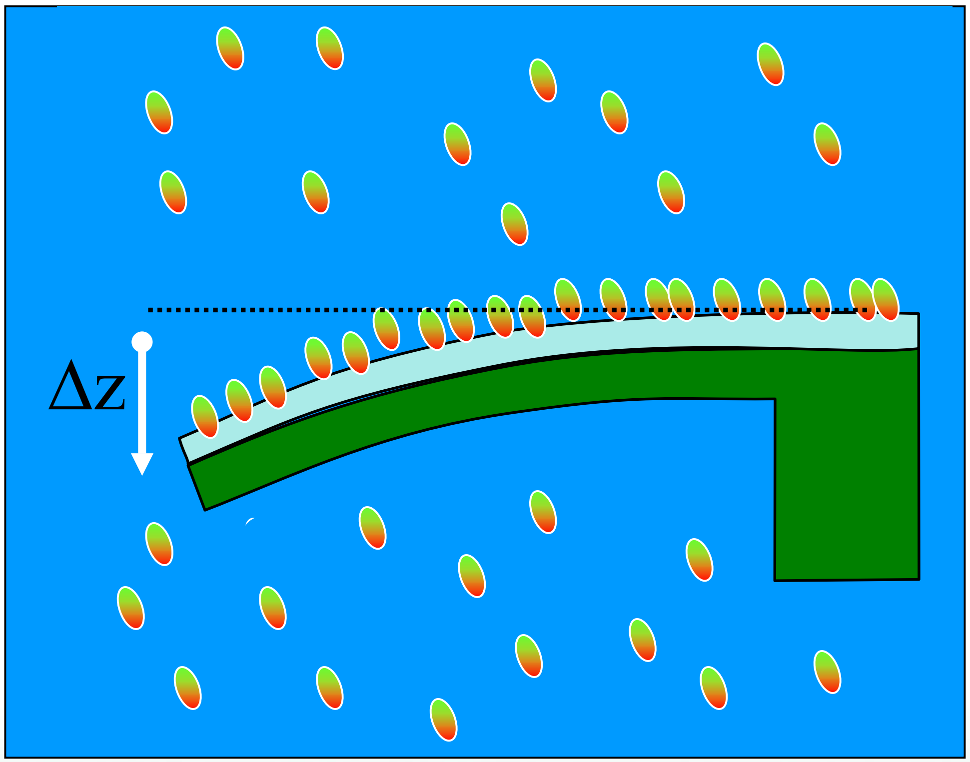
Topics:

- Fundamental MC response principles and limitations
  - *MC morphology modifications*
  - *Optical bending differential readout*
- Selectivity issues
  - *New receptor phases and multiple MCs*
  - *Combining with SERS*
- Performance evaluations throughout talk

Cantilever-Based Chemi-Mechanical Transducer

Demonstrated applications:

gas & liq. sensors	metal ions
VOCs	pH
DNAPLs	etc.



Stoney's Equation:

$\Delta\sigma$ - differential stress
Y - Young's modulus
ν - Poisson's ratio
l - length
t - thickness

$$\Delta z = \frac{3l^2(1-\nu)}{Yt^2}\Delta\sigma$$

What are the limitations?

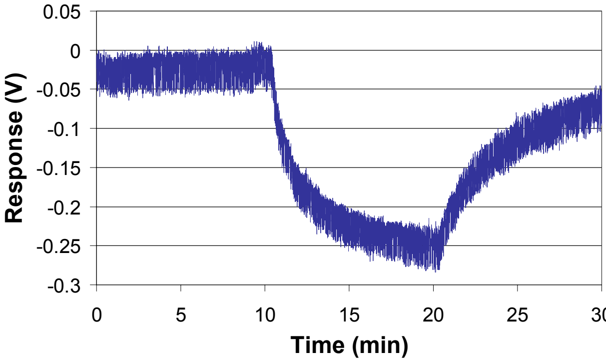
Surface stress (σ) modulation *is limited by initial interfacial energy (γ)* of interface

Shuttleworth Eq. → $\sigma = \gamma + \frac{d\gamma}{d\varepsilon}$

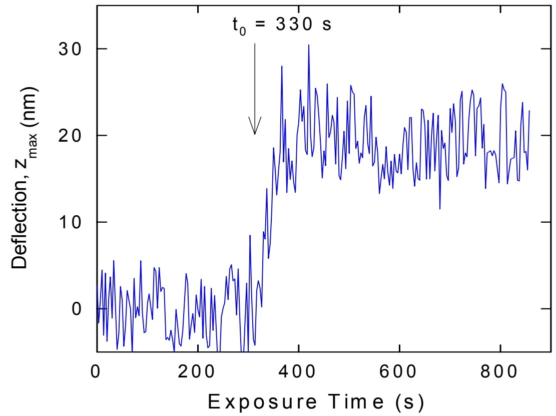
- **Interfacial energies for most solids in water are rarely above 100 mN / m**
- **Organic modifying coatings *further reduce* interfacial energy**

Multi-Parameter Signal Detection (Individual Parameters)

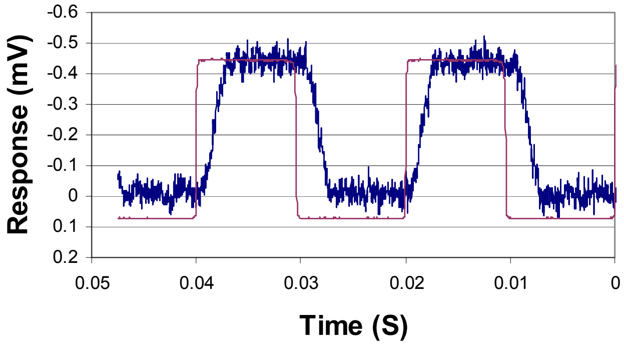
Chemical



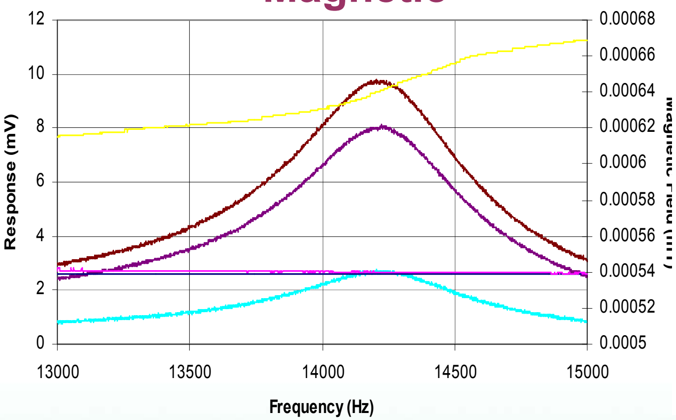
Nuclear



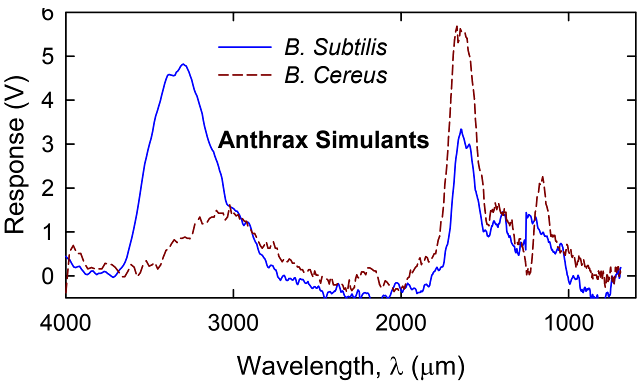
Infrared



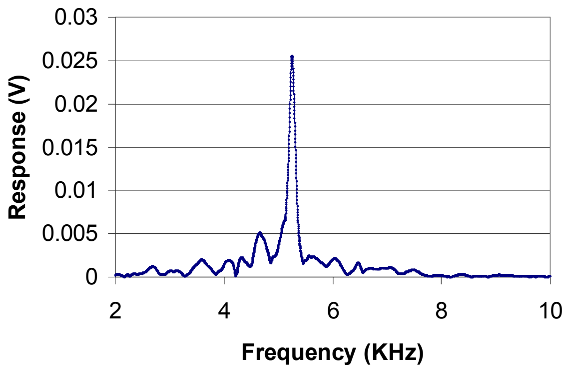
Magnetic



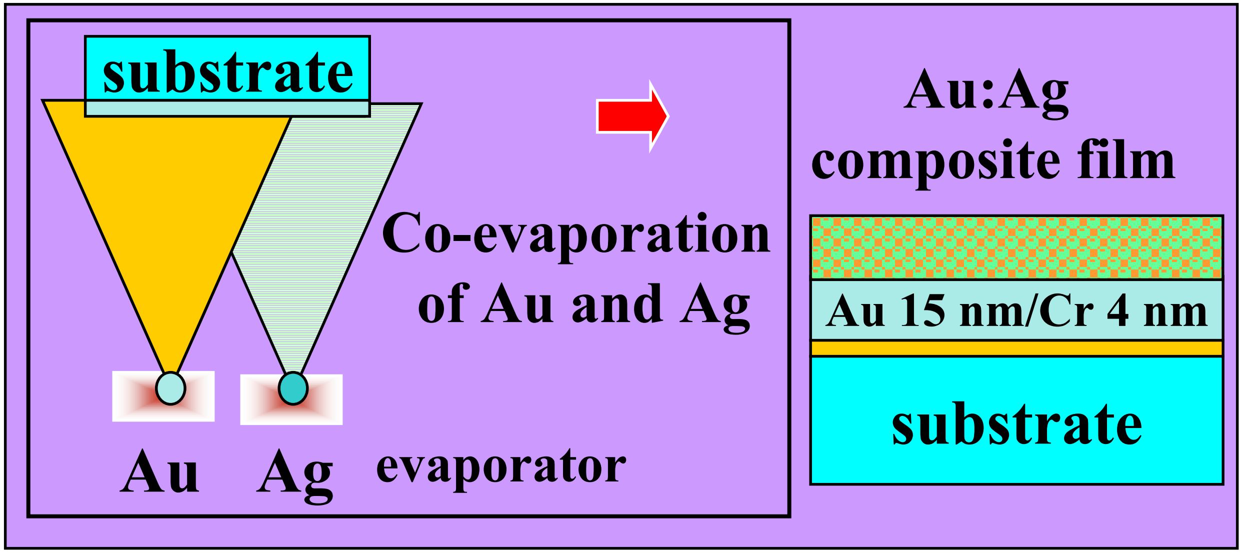
Biological

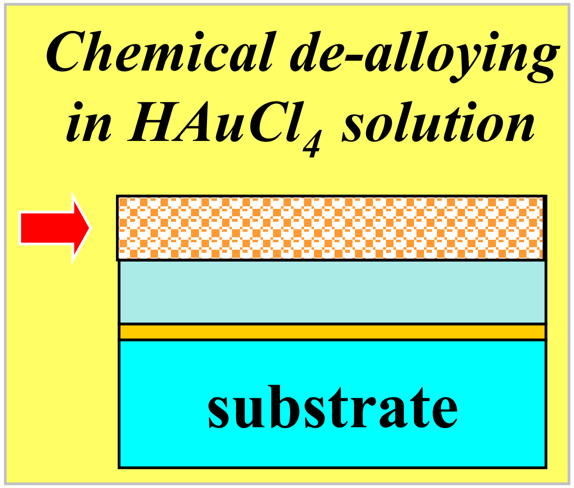


Acoustic



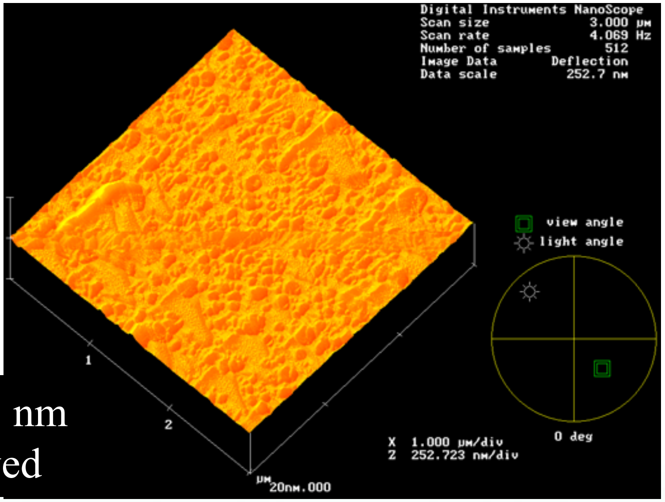
"Dealloying" Nanostructuring Strategy





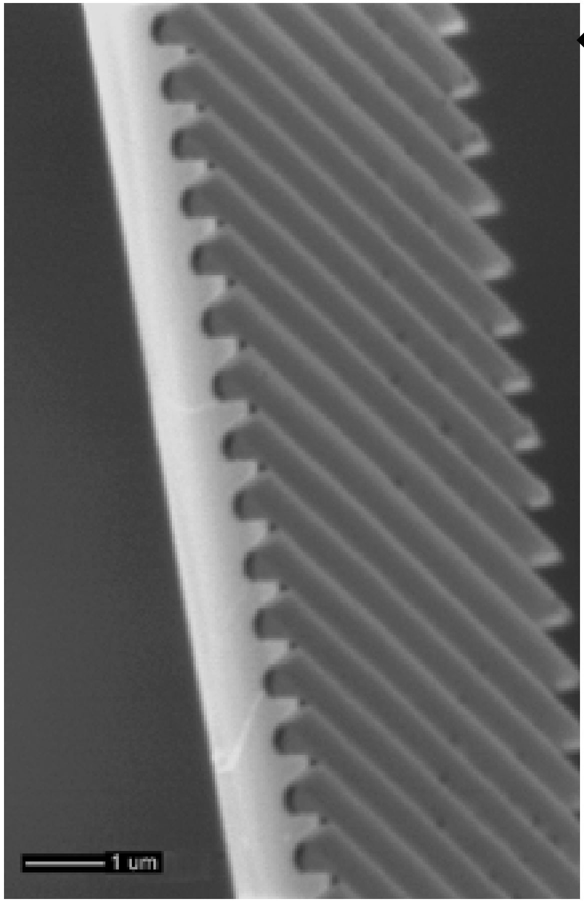
Advantages

- ***Standard vacuum PVD process***
- ***Continuous range of thickness possible***
- ***Short processing time***
- ***SERS active surface ? →***



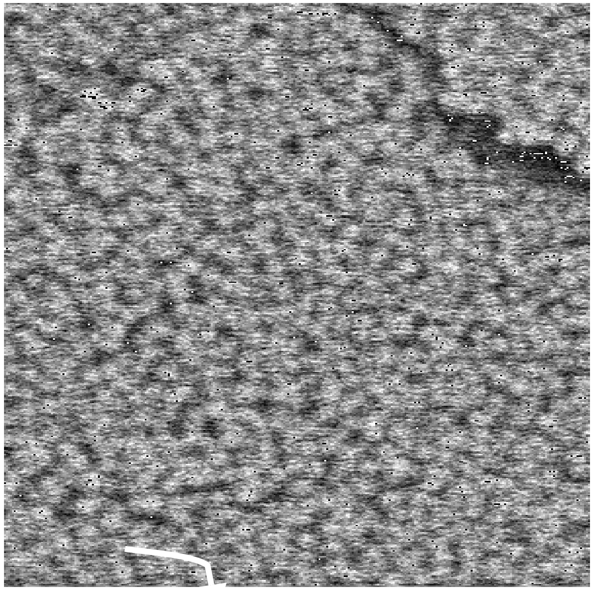
RMS roughness – 35 nm for 50 nm dealloyed

Other Nanostructuring Strategies

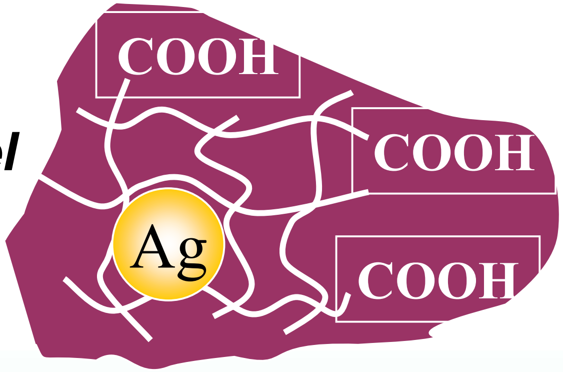


← ***Focused ion beam modified cantilevers with enhanced, stable response***

Metal – organic (e.g., polymer) composite phases →



For example, Ag impregnated hydrogel

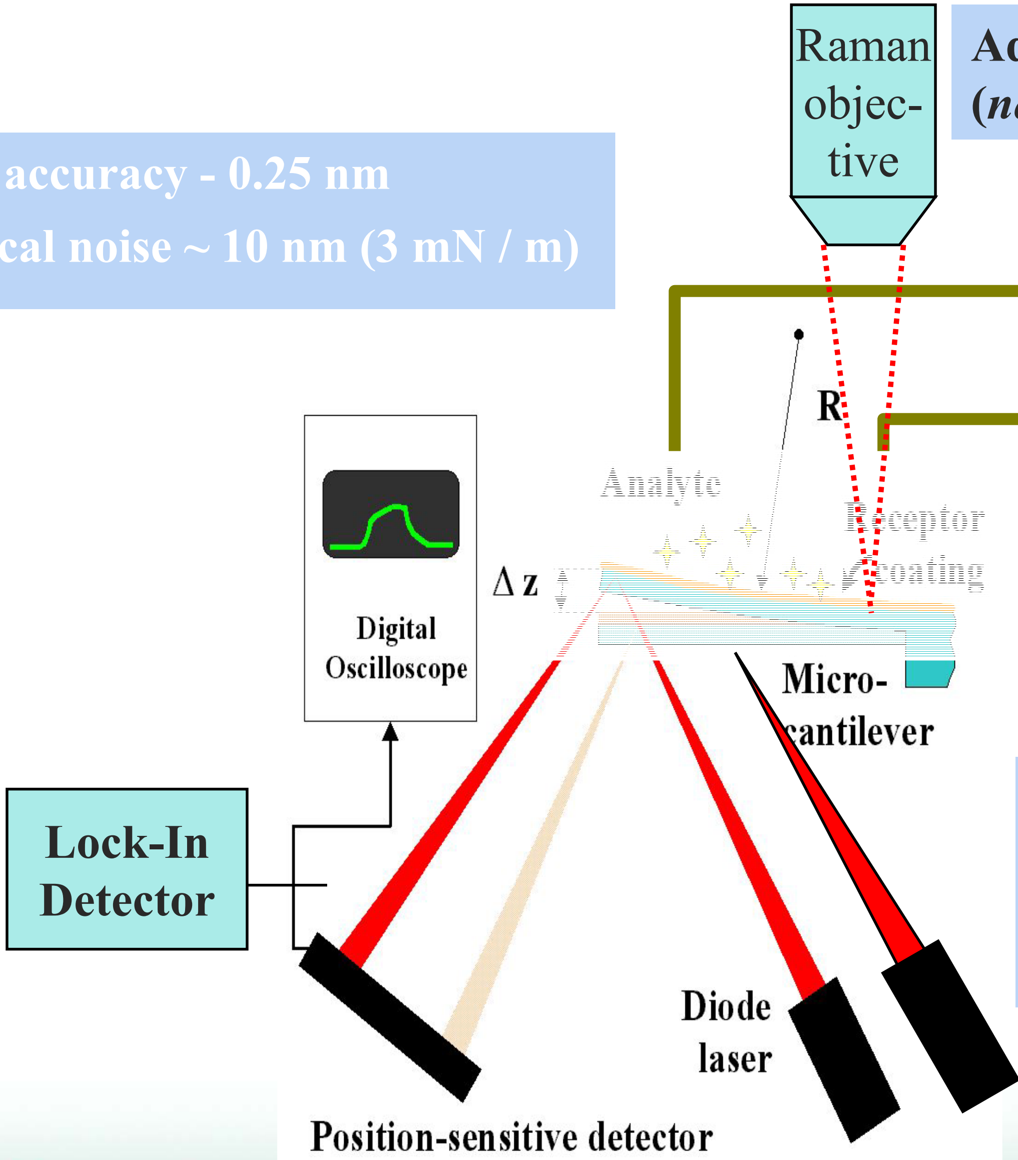


Microcantilever Deflection Measurements

Add SERS capabilities
(*new element of selectivity*)

Readout accuracy - 0.25 nm

Mechanical noise ~ 10 nm (3 mN / m)



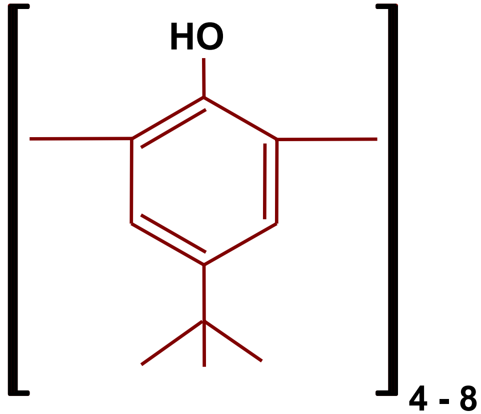
Cantilever mounted in a 100μL flow cell

Flow rate:
0.15 mL/min (liq.)
to 3 mL/min (gases)

Add differential design to reduce noise/drift
(*more robust for demanding sensing applications*)

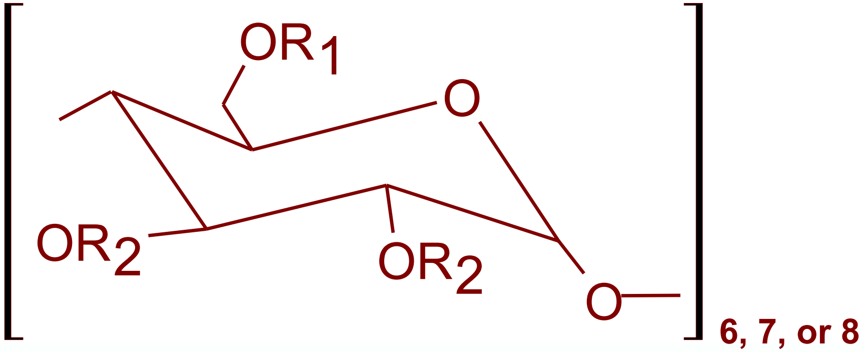
Working Toward Greater Selectivity Via Creation of Different Phases for MC Arrays

Among the phases under Investigation are the tert-butyl (& other volatile) calixarenes →

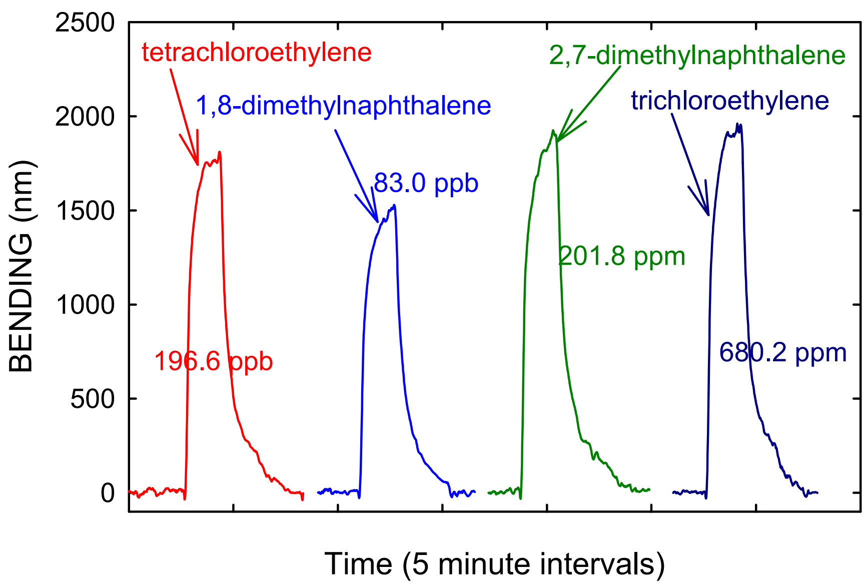


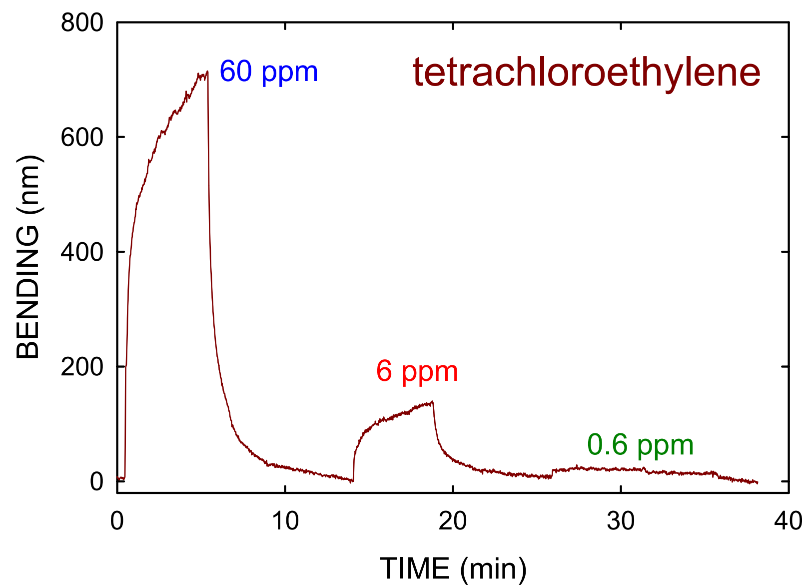
And a family of hydrophobic and, thermally stable cyclodextrins (CDs) that we have synthesized →

These phases are particularly useful because of the molecular recognition properties of macrocycle receptors and their amenability to PVD onto MCs

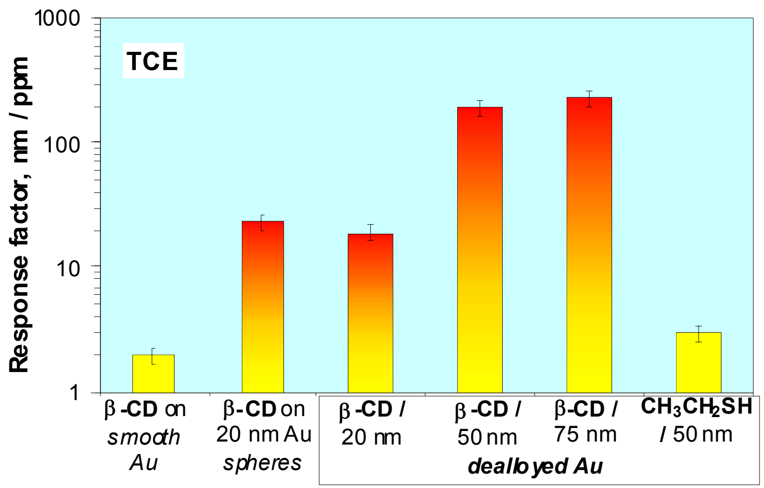


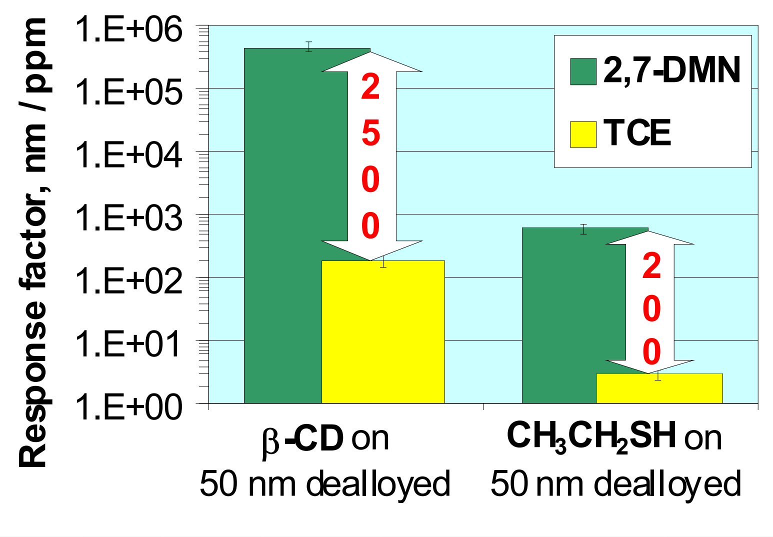
Chemical Detection Using -cyclodextrin and Calix[4]arene Coatings





Nanostructured versus Smooth Surfaces





Gas-Phase Analytes: SAM of β-CD

17-fold increase in surface area

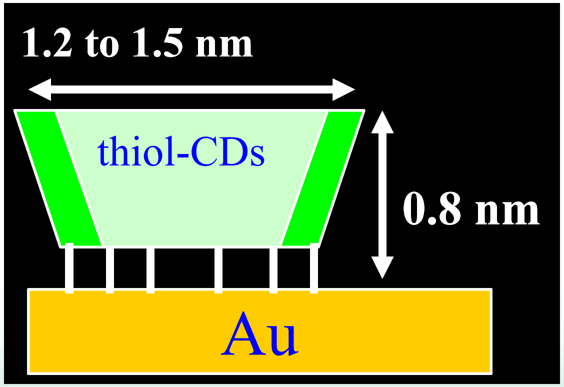
(50nm dealloyed vs smooth)

100-fold signal enhancement

LOD for 2,7-DMN of 140 ppt

Nanostructuring influences selectivity

Cavitand shows greater selectivity



Results: SAMs / Films of: Synthetic CD (HDM-β-CD), Liquid-Phase Analytes

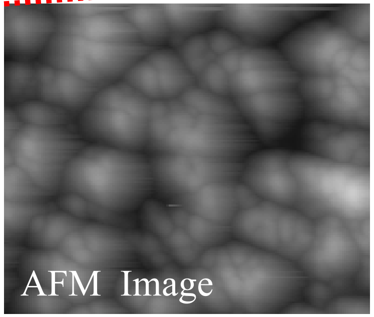
Compound \ ppm	SAM (smooth)	SAM (nano)	17 nm (smooth)	17 nm (nano)	50 nm (nano)
2,3-DHN	290	4.8	31	0.99	0.025
2,7-DHN	250	7.5	39	1.0	0.039
Tolazoline	300	17	214	13	4.9
Benz. Acid	1500	140	250	42	18

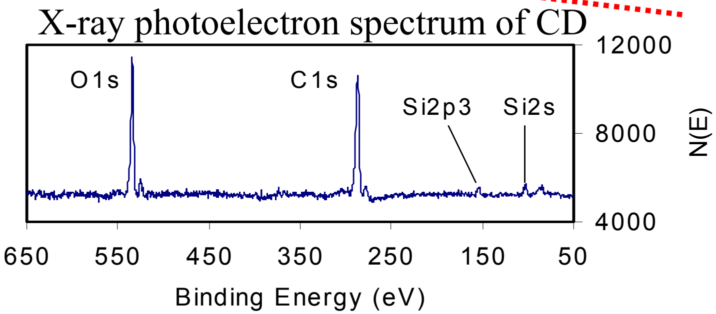
Dramatic improvement in LODs (in ppm) with:

- ***nanostructuring***
- ***thicker films***

With the 50 nm film:

- ***underlying gold is completely covered***
- ***surface is irregular***



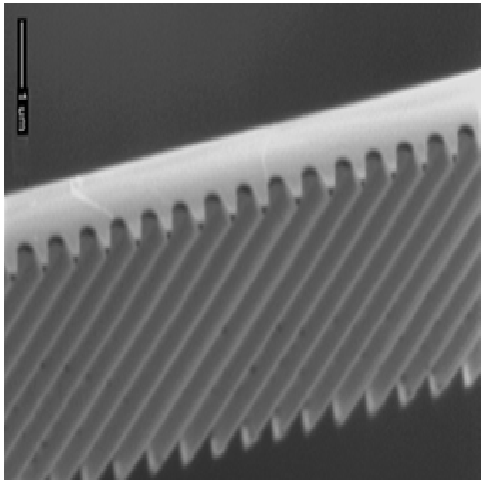


Compound \ nm/ppm	Calix[4]	Calix[6]	Calix[8]	HDM-β-CD
2,2'-PCB	240	83	44	52
TCE	0.14	5.7	2.6	0.81
8-HyQuinoline	2.0	1.9	3.7	1.5

***Results:* Response Factors Vary With Film Type and Class of Analyte**

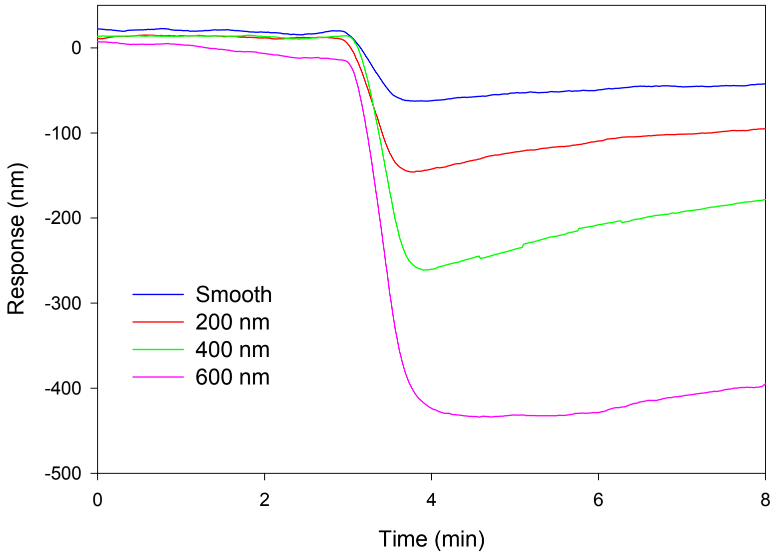
Response factors shown in nm / ppm

Performance of "Nano-Grooved" Cantilevers

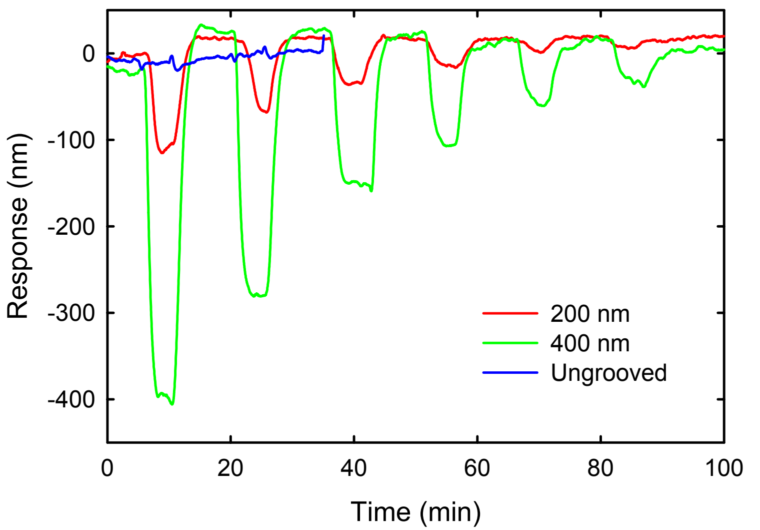


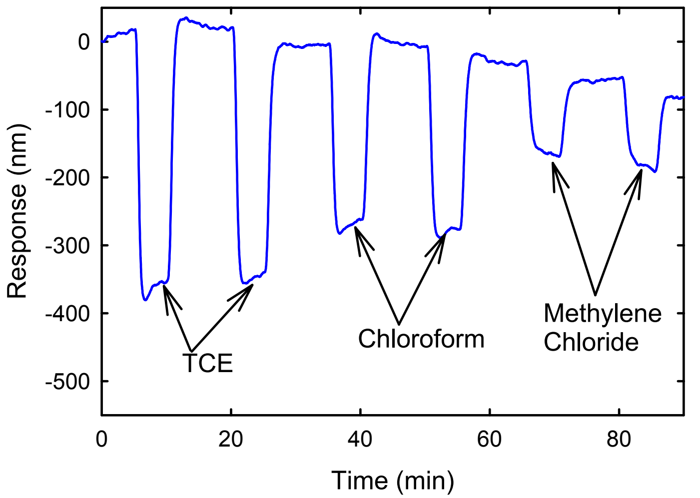
Responses to various VOCs

***Thinning the structure* (TCE)**



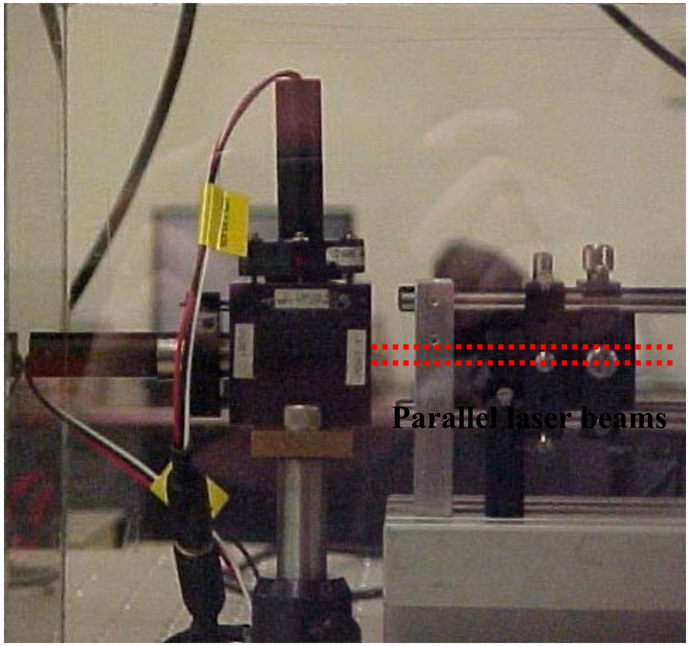
***Effect of the grooves* (DHN)**

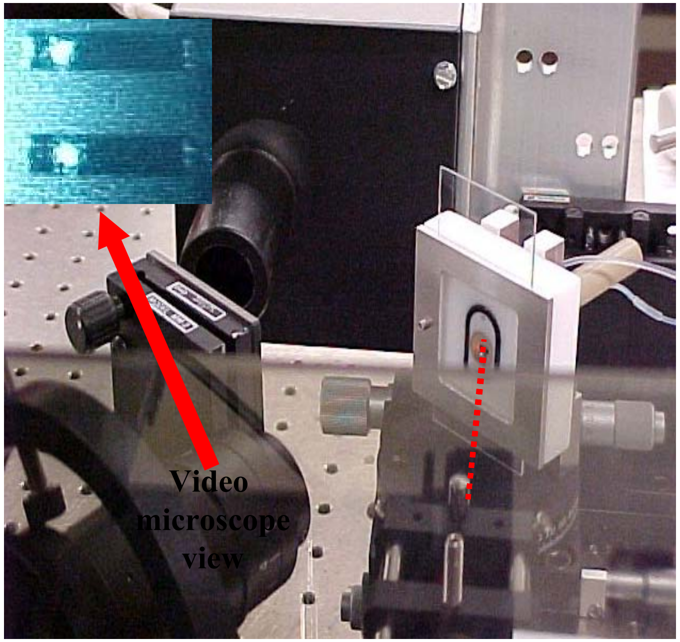




LOD for TCE in mid ppb range

Design and Evaluation of a Differential MC System





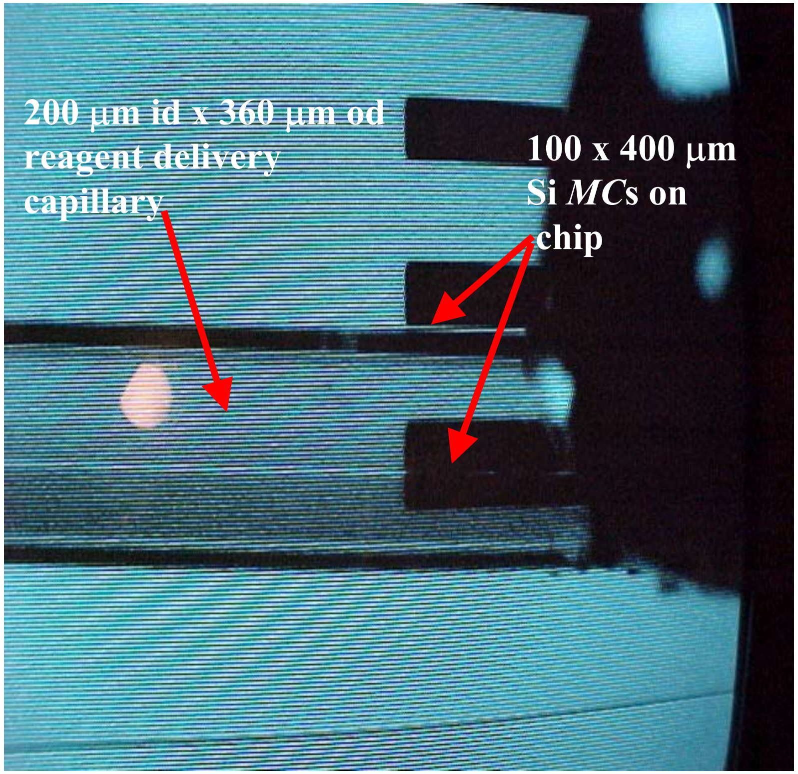
Measurements using single cantilevers are compromised by various sources of noise or baseline drift (see below), but these can be reduced through implementation of a differential detector design.

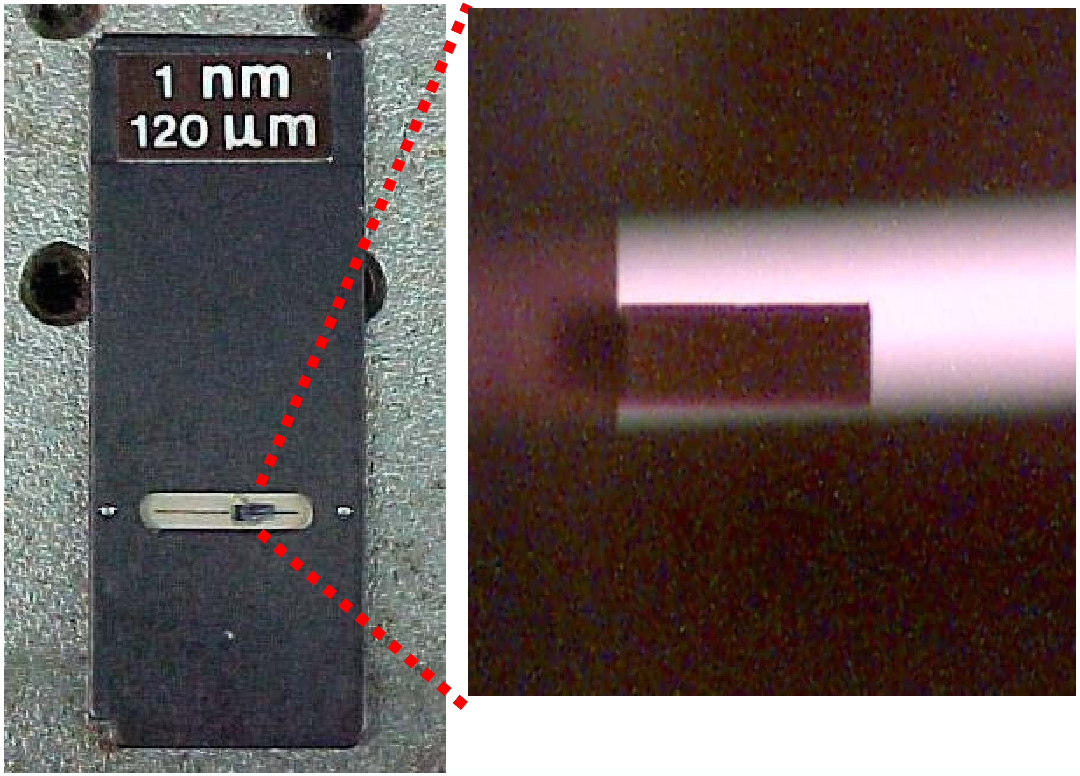
-Thermal; - Refractive index; - Ionic strength;
- Flow rate; - Mechanical

Methods of Individually Coating MCs in an Array

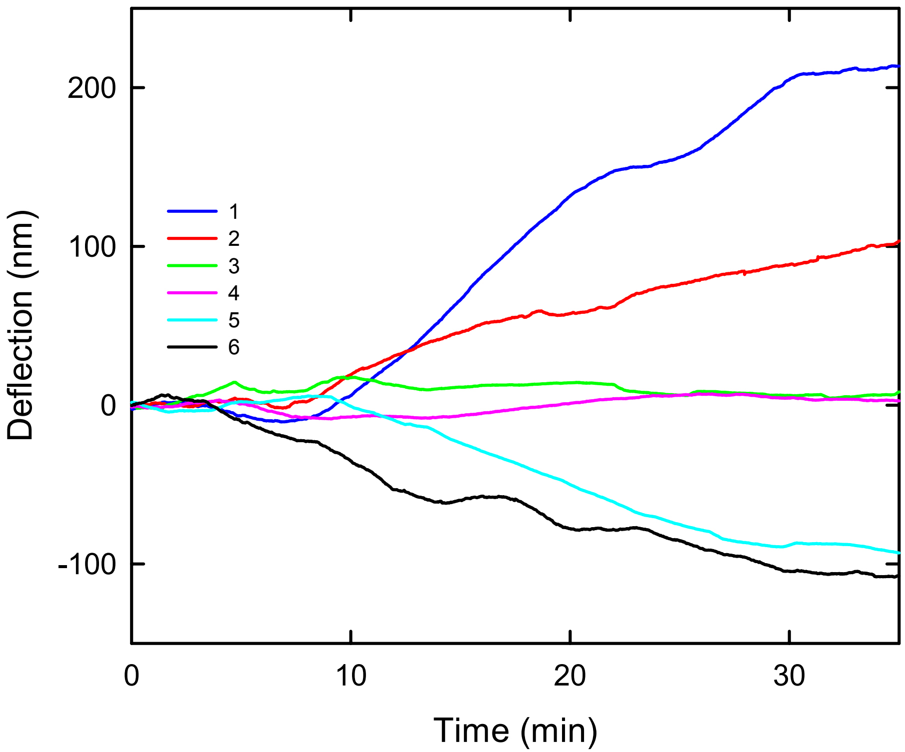
Liquid phase reactions; e.g., thiolated CDs

Physical vapor deposition through mask of volatile receptors; e.g. calixarenes





Chiral Discrimination Using Cantilevers



1 – 50 mg/L L-tryptophan (anti-L-AA)

2 – 50 mg/L L-phenylalanine (anti-L-AA)

3 – 50 mg/L D-tryptophan (anti-L-AA)

4 – 50 mg/L D-phenylalanine (anti-L-AA)

5 – 50 mg/L L-phenylalanine (IgG)

6 – 50 mg/L D-phenylalanine (IgG)

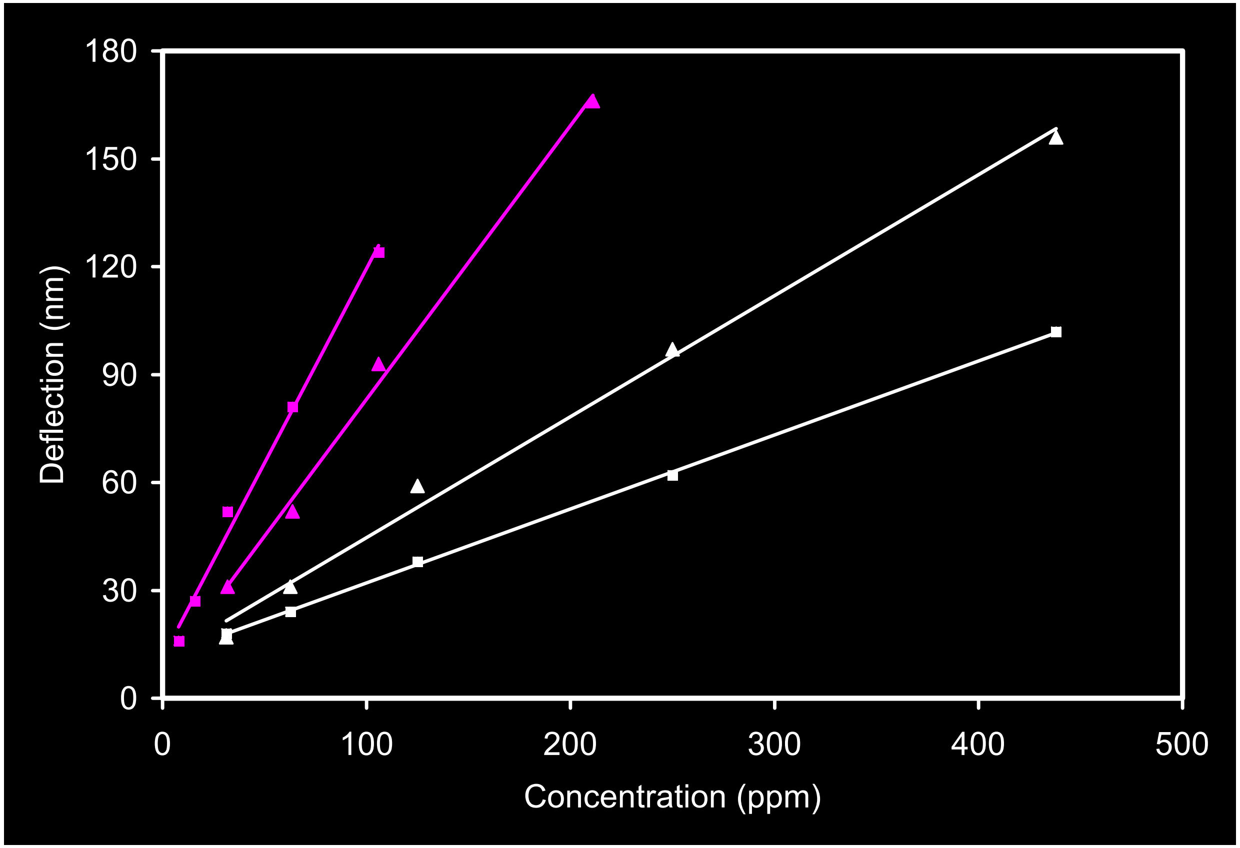
Quantitation of Species in a Mixture Using Cantilevers

Quinoxaline (white)

8-hydroxyquinoline (pink)

Calix[6]arene (triangles)

Calix[8]arene (squares)

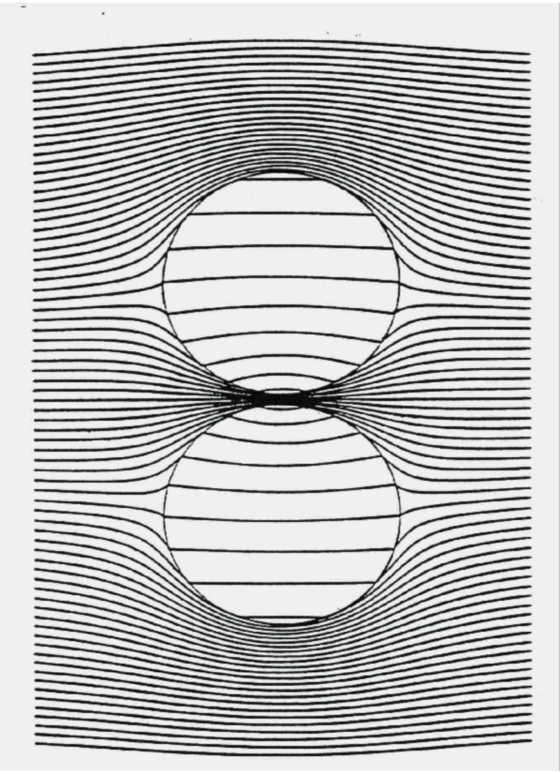


Differential response between a 140 nm calixarene coated lever and an untreated lever.

Selectivity: Hybrid MC-SERS Sensors

Rational for Adding SERS Capability to MC Sensors

-Environmental and biomedical applications
 cancer diagnosis, remote sensing, etc
- Complimentary modes of selectivity
 specificity of receptor binding (MC)
 vibrational signatures (SERS)
- Common features
 microscopic areas probed by laser
 enhanced response with nanostructuring



Basis of Large Raman Surface Enhancements

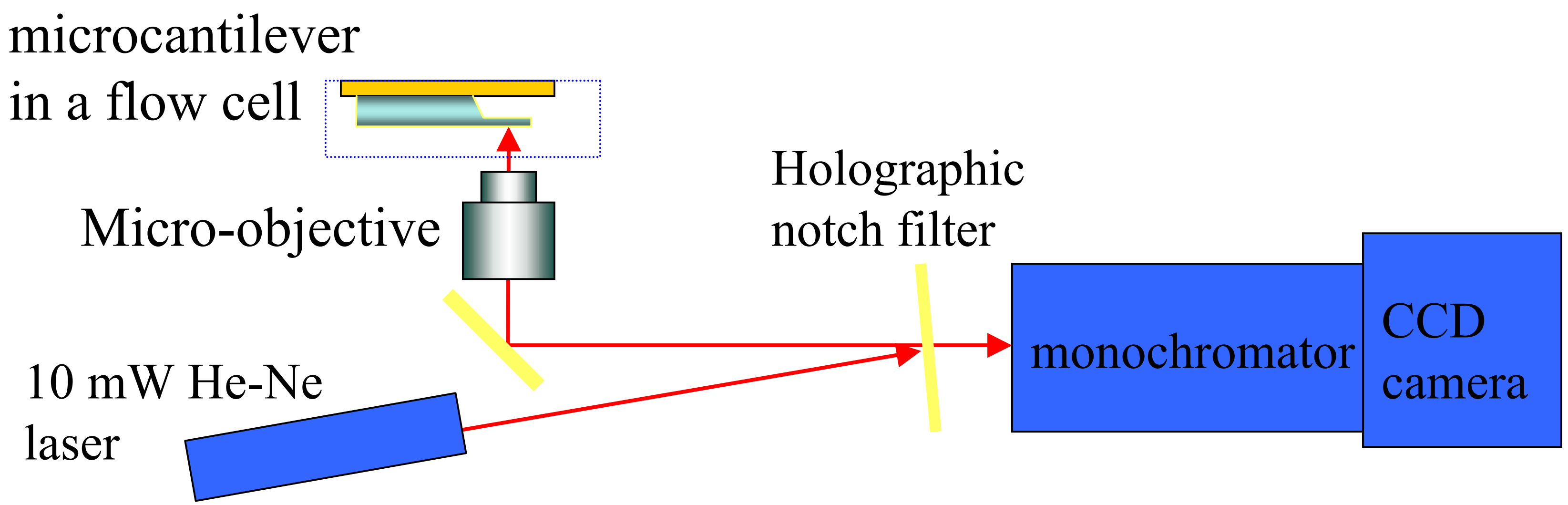
- Raman signals proportional to field ~ 10^4

- Closely spaced metal nanospheres (or other shapes) can generate large enhancements of incident fields due to concerted plasmon field effects (EM Model)

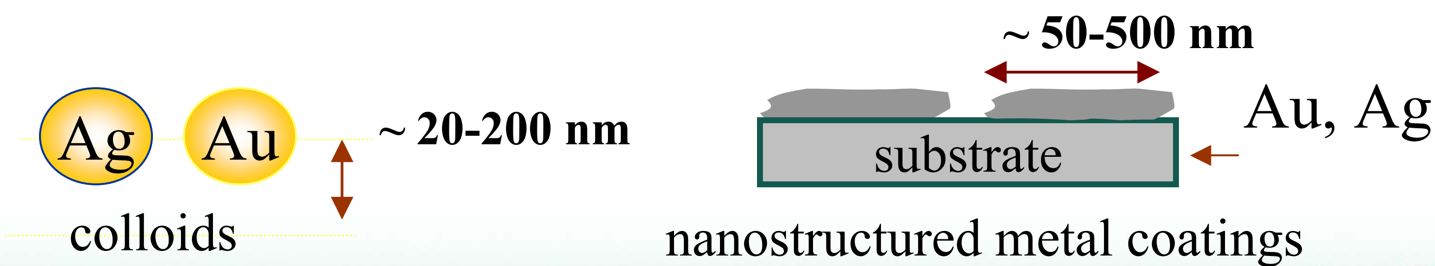
- Interactions between analytes and metal can influence the analyte polarizability (Chemical Model)

Hybrid MC-SERS Sensors; Acquisition of Spectra

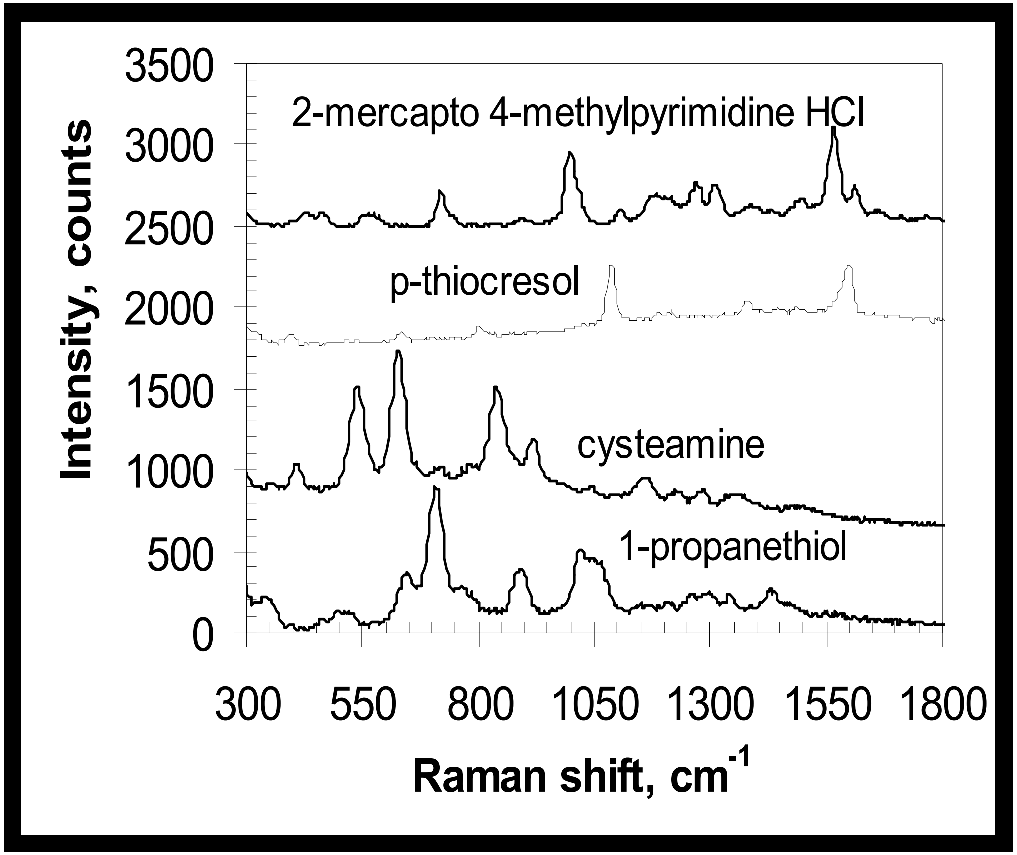
- *Optical arrangement*



- ***SERS - active objects (MC nanostructured surfaces !)***



Hybrid MC-SERS Sensors



Dealloyed gold surface Overcoated with silver

- *Gold or Silver coated MCs show strong responses to thiolated compounds*
- *Significant improvements in SERS signals are observed when dealloyed gold surfaces are overcoated with a layer of silver*
- *Distinctive (easily distinguishable) vibrational spectra are observed when such surfaces are exposed to thiolated compounds*

Hybrid SERS-MC Sensors

SERS spectra obtained on the nanostructured surfaces used in MC work with polyaniline adsorbed on the MC→

1 - a traditional silver island film

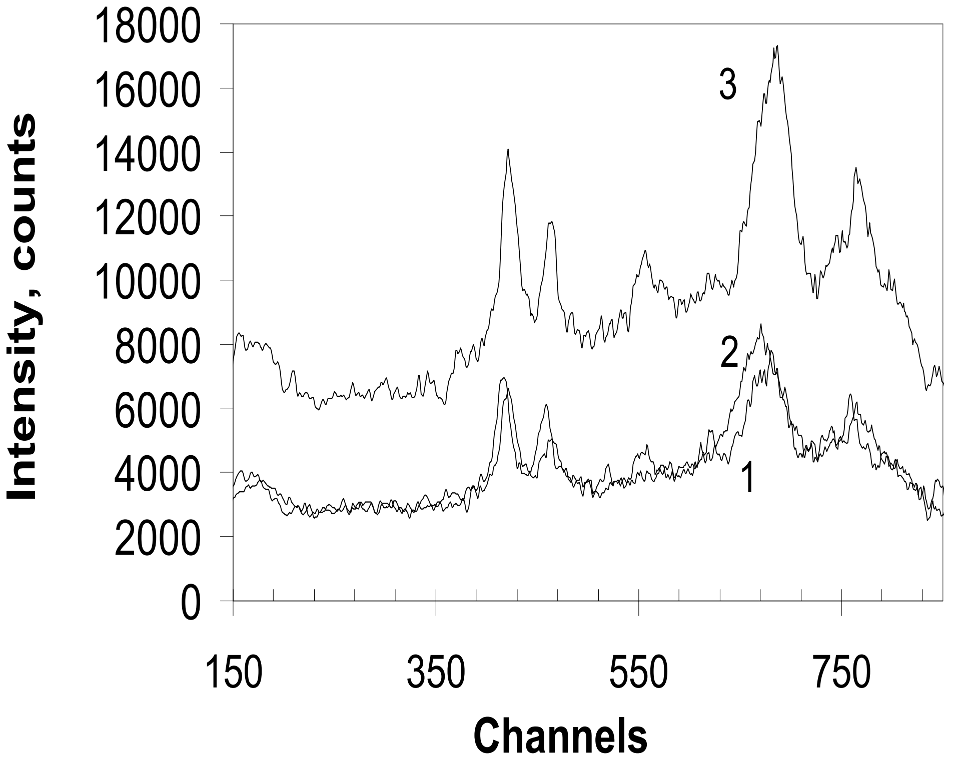
2 - 50 nm dealloyed gold

3 - gold nanobeads assembly

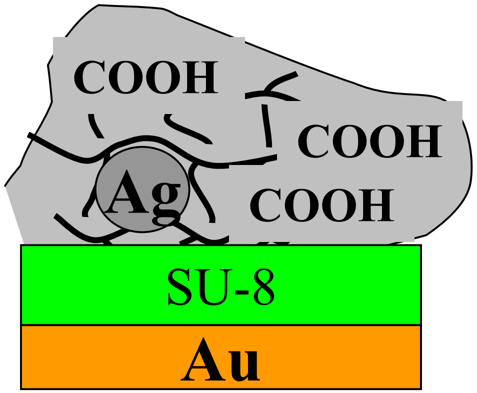
Experimental:

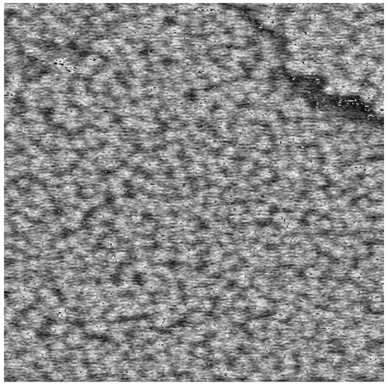
Kr^{+} laser 5 mW at 647 nm,

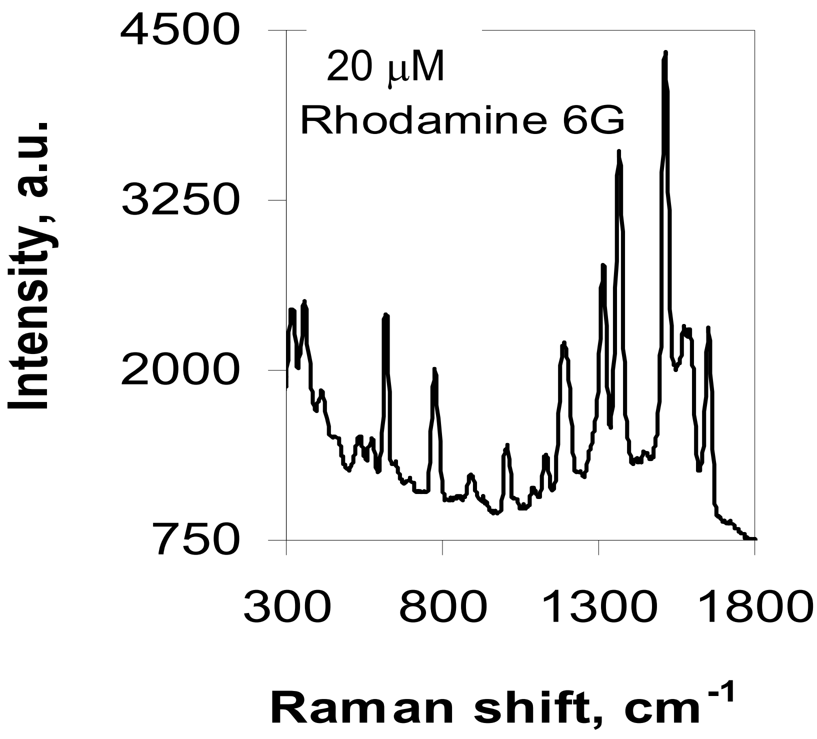
Confocal arrangement with low resolution modular Raman apparatus



Hybrid MC-SERS Sensors: Silver Nanoparticle Modified Gels







MC Responses

(Nanostructured surface with
<u>CD-Ag composite thin film):</u>
50/50 mixture gives essentially same response and is indistinguishable. However, SERS spectra obtained on our *MC* show unique features to each compound

Concluding Remarks

→ **Developed technological approaches to integrated sensor - actuator hybrids**

→ **Identified promising multifunctional nanostructured coatings:**

- "dealloyed gold"
- poly-hydroxyethyl methacrylate (pHEMA) hydrogels

→ **Implemented multi-modal functionality of *MC* transducers:**

- pH measurements: 1 to 25 μm / pH unit ! (platform for enzymosensors)
- LODs in ppt for some analytes using cavitand receptor phases
- SERS signatures of chromophores, thiols, and nucleotides