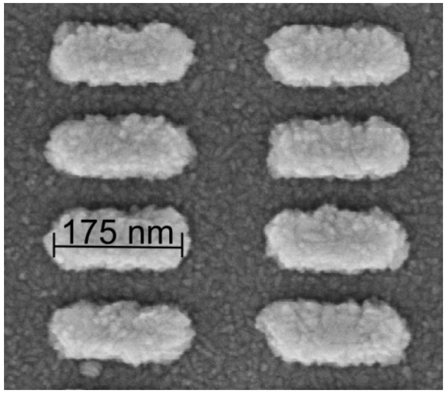
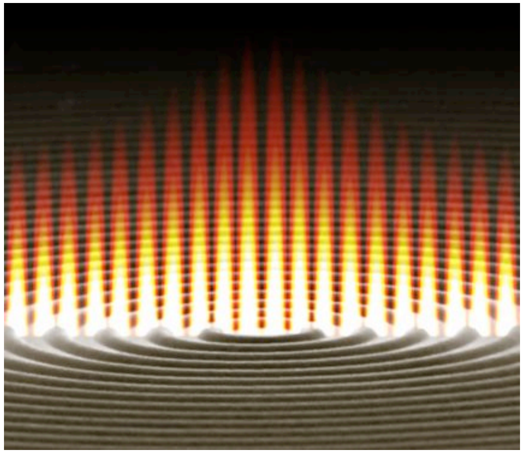


Carpenter Group, CNSE



Oh group, University of Minnesota

Heat-activated Plasmonic Chemical Sensors for Harsh Environments

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College of NanoScale Science and Engineering
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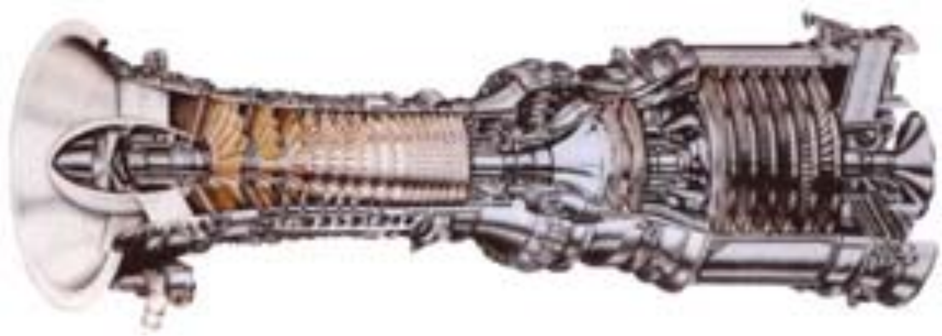
6/11/13

Harsh Environment Chemical Sensors

Need for new sensing technologies to meet the requirements for zero emission energy sources

Nanocomposite Materials

- Optical analysis of Au SPR bands
- YSZ, TiO_2, CeO_2 matrix materials
- 500-800°C operating environment
- SOFC, Jet engines, turbines
- CO, H_2, NO_x, R_xS

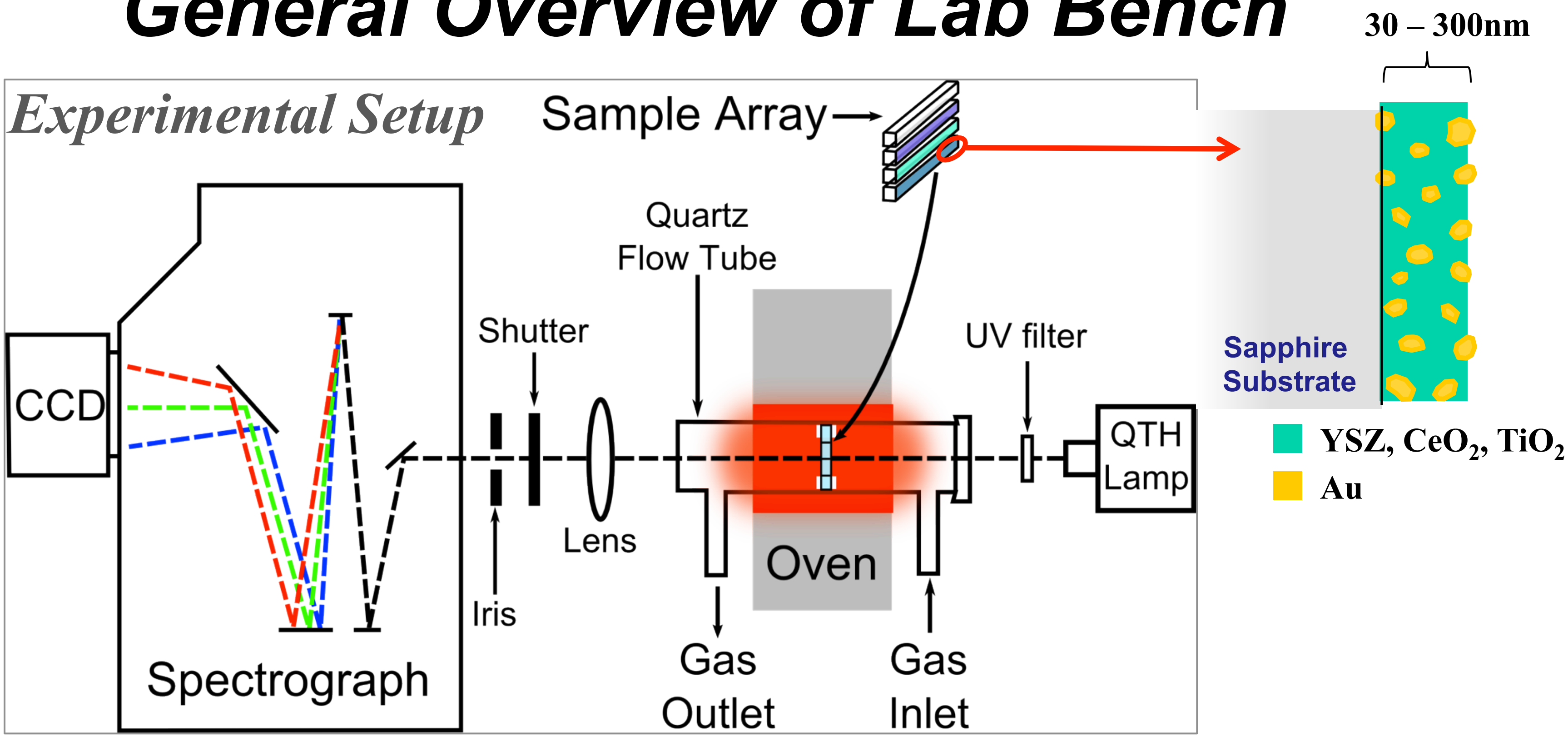


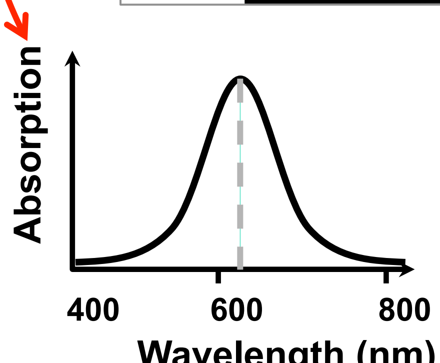
Goals of Research are Two-Fold

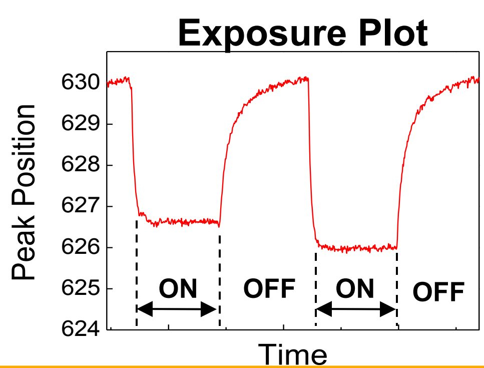
1. Develop prototype nanorod materials for use in next generation sensing devices
   - Sensitivity, reliability, selectivity
2. Design and develop bulls-eye energy harvesting structures

Why do we need energy harvesting?

General Overview of Lab Bench







This is too complex for integration…

YSZ = Yttria Stabilized Zirconia

The Concept: Combine energy harvesting bulls-eyes with patterned nanorods

Heat activated plasmonic based chemical sensor

(1) Bulls-eye

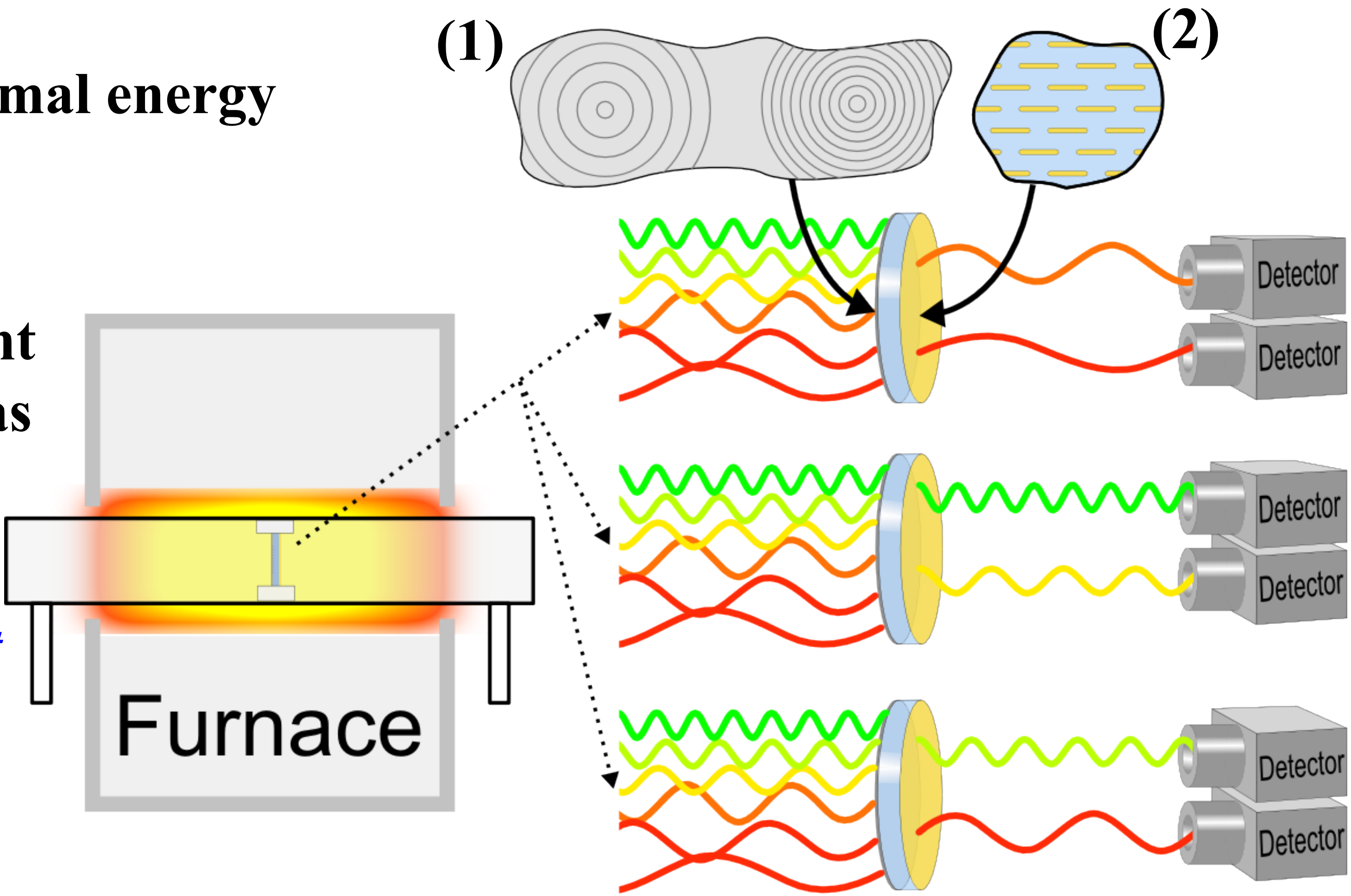
- Absorbs thermal energy
- Emits light

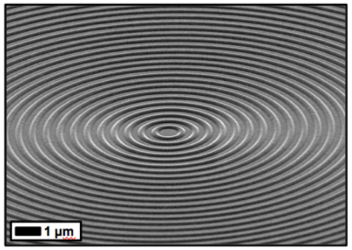
(2) Nanorods

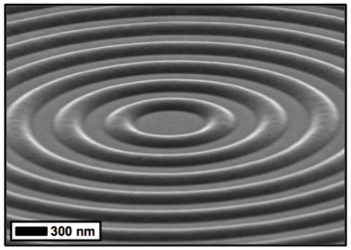
Transmitted light dependent on gas exposure

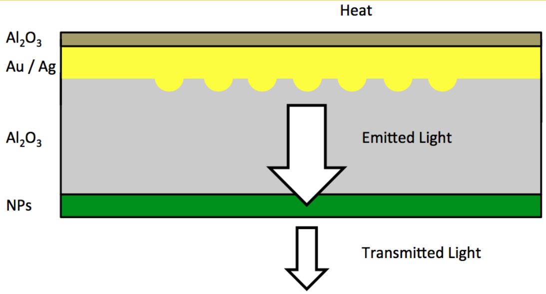
No external light source required

No expensive detectors needed





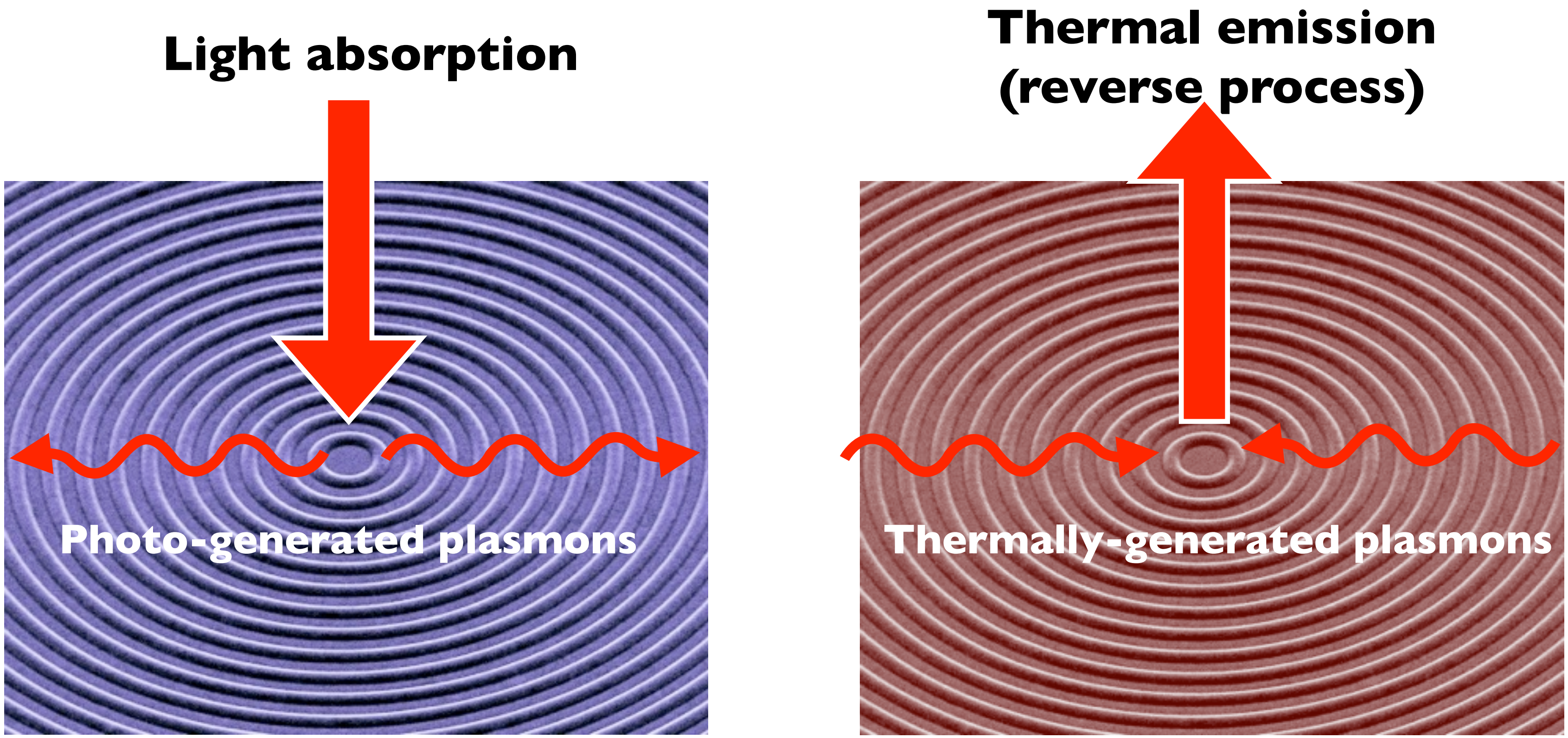




Research Objectives:

1) Optical modeling of both nanorod and energy harvesting plasmonic devices (FDTD)
2) Development of e-beam patterned arrays of Au nanorods embedded in metal oxide matrices with optical responses in the 600 nm to 1200 nm range.
3) Design and development of a plasmonic energy harvesting light source.
4) Stability and selectivity testing for the detection of target gases in the presence of interfering species. Principle component analysis (PCA)
5) Development of a single wavelength sensor testing station
6) Design of packaging details

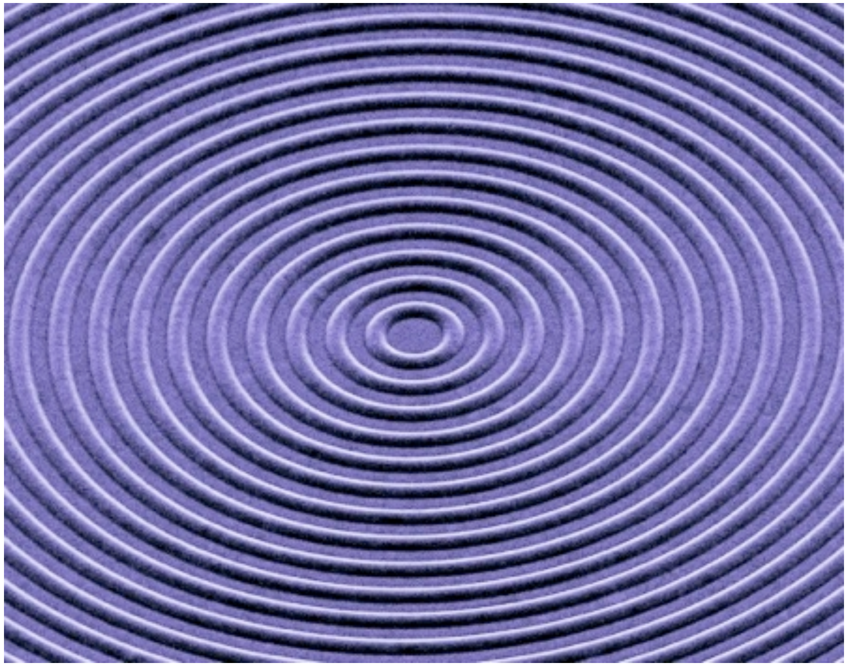
Bulls-eye Basics: Thermal Excitation of Plasmons

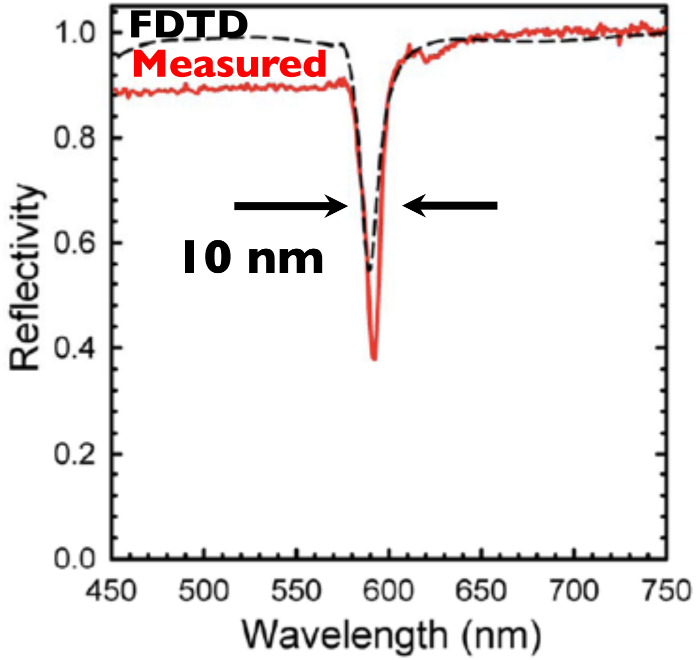


- According to Kirchhoff's law, emissivity = absortivity.
- Plasmonic structures such as metallic gratings, bull's eye etc. can modulate optical absorption. Conversely, they can also tailor thermal emission at higher temperatures, via converting thermally generated plasmons to light.

Smoothness vs. Resonance Linewidth

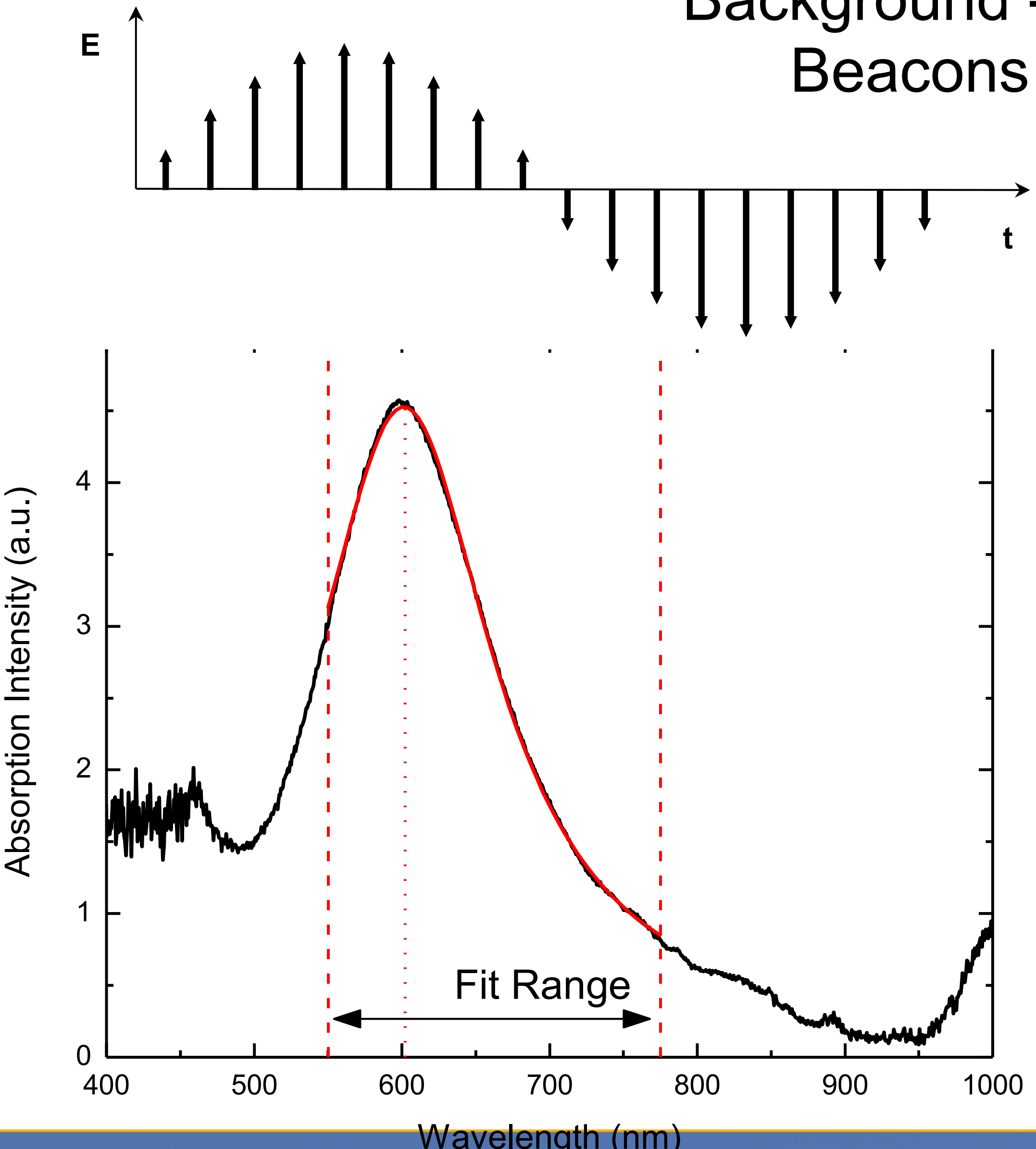
Nagpal, Lindquist, Oh & Norris, ***Science*** 325, 594 (2009)

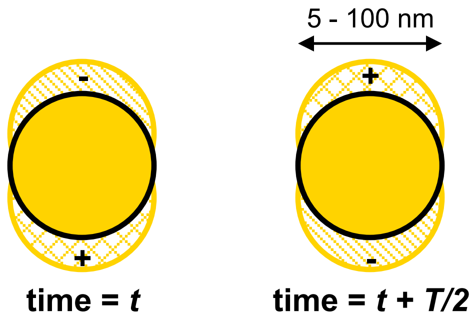




- **Resonators and gratings with ultra-smooth surfaces show sharp plasmon peaks**
- **Template-stripped Ag bull's eye shows a sharp and directional absorption dip with the linewidth below ~10 nm.**
- **The same structure made by direct FIB milling showed a broader and much weaker peak.**

Background - Au Nanoparticles as Optical Beacons For Transduction Events





$$\Omega = \sqrt{\frac{Ne^2}{\left(1 + 2\varepsilon_m + \chi^{ib}(\Omega)\right) m_e 4\pi\varepsilon_0 R^3}}$$

Ω - SPR Frequency

N - free electron number

m_e - electron mass

ε_0 - permittivity of free space

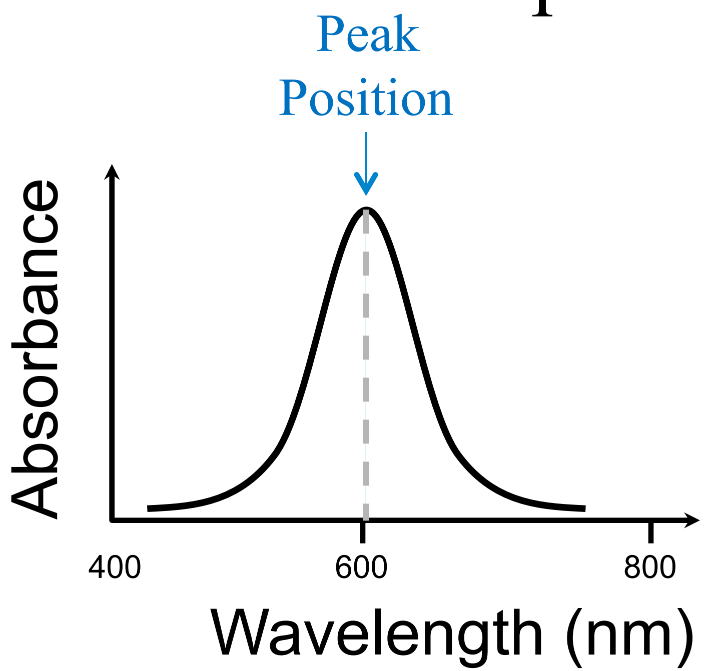
ε_m - matrix (YSZ) dielectric constant

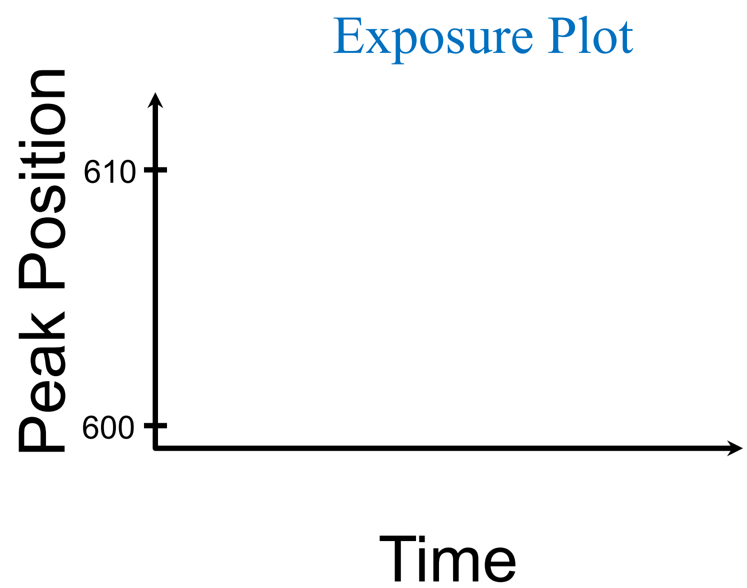
$\chi^{ib}(\Omega)$ - Interband trans. dielectric const.

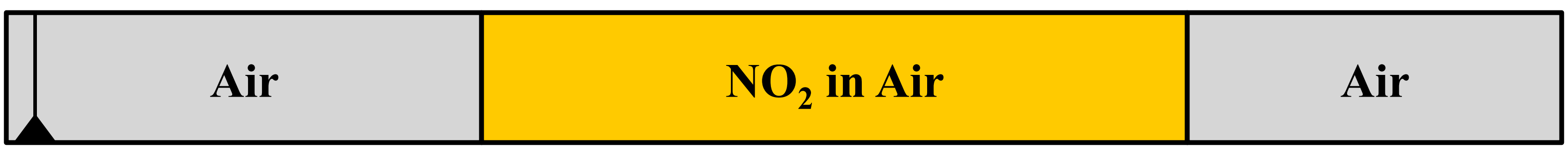
R - particle radius

Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer, Berlin, 1995

Example of Data Acquisition







$$\Delta\Omega \propto \Delta\sqrt{\frac{N}{(1+2\varepsilon_m)}}$$

H_2, CO — Reducing

NO_2 — Oxidizing

Selectivity Challenge

How to Discriminate Between Gases?

Data Analysis
(extract selective information)

- Principal Component Analysis
- Linear Discriminant Analysis
- (Neural Networks, Cluster Analysis…)

Exposure Conditions

- Temperature

Materials
(influence selective reactions)

Metal Oxide

- YSZ
- TiO_2
- CeO_2

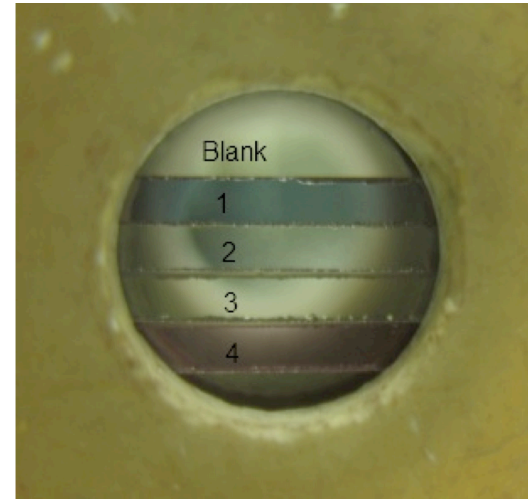
Gold Particles

- Size
- Shape

Sensor Array Studies

Element 1: **MBE grown CeO_2 with implanted gold**

- Ceria is 200nm thick
- Gold is implanted to depth of ~75nm
- Post annealed to 1000°C
- Gold particle size ~30nm
- Au ~ 8 at. %



Element 2: **PVD Au-YSZ**

- ~30nm thick Au-YSZ
- Au particle size ~25nm
- ~10 at.% Au

Element 3: **PVD Au-TiO_2**

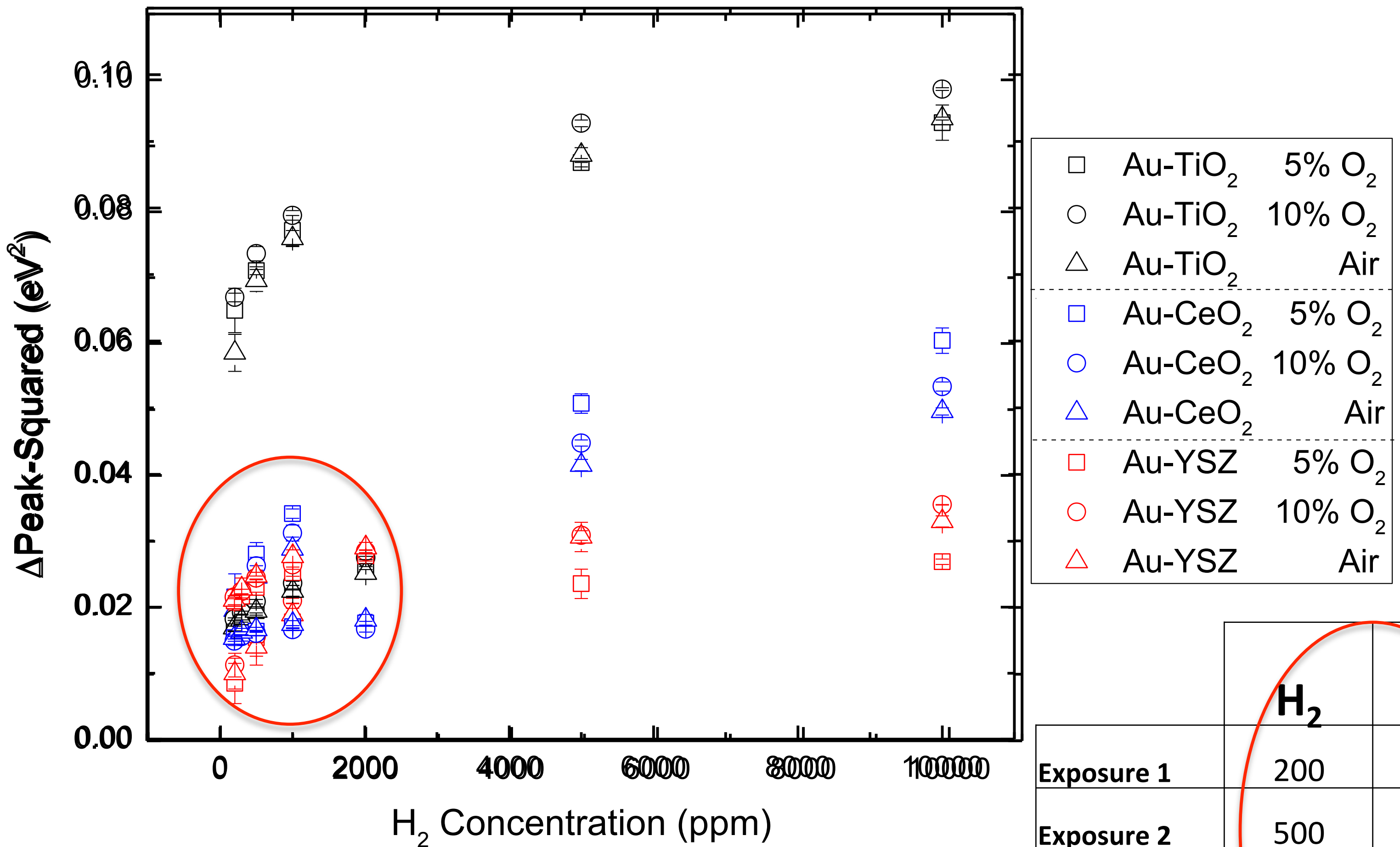
- ~30nm thick Au-TiO_2
- Au particle size ~25nm
- ~10 at.% Au

500°C

	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98

- **Simultaneously Compare Sensing Characteristics**
- **PCA performed for Selectivity**
- **Detailed analysis to be completed for sensing mechanism analysis**

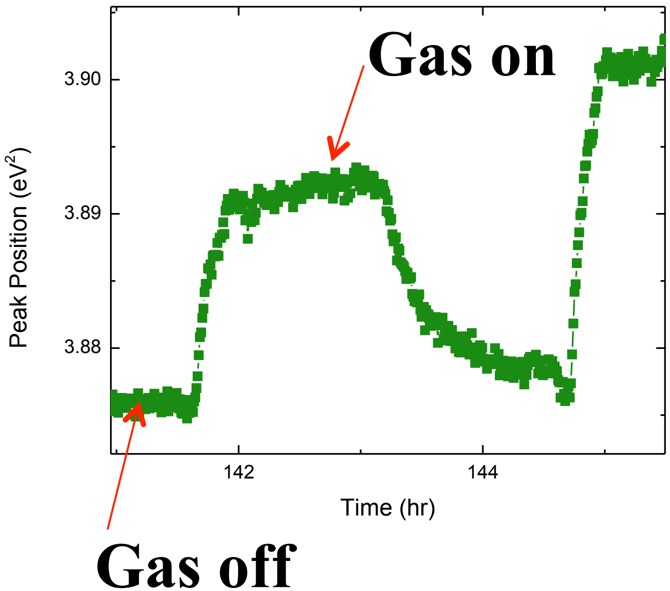
H_2 ΔPeak vs Concentration

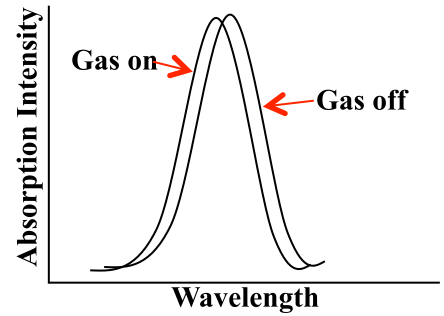


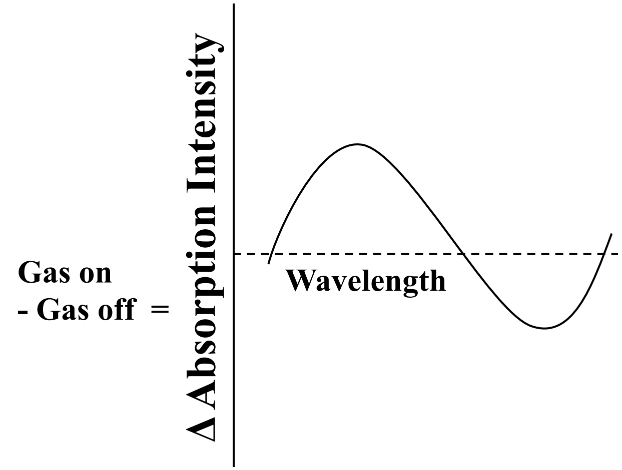
	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98

Challenging selectivity issues for CO and H_2!

Sensor Array Analysis: Applying PCA





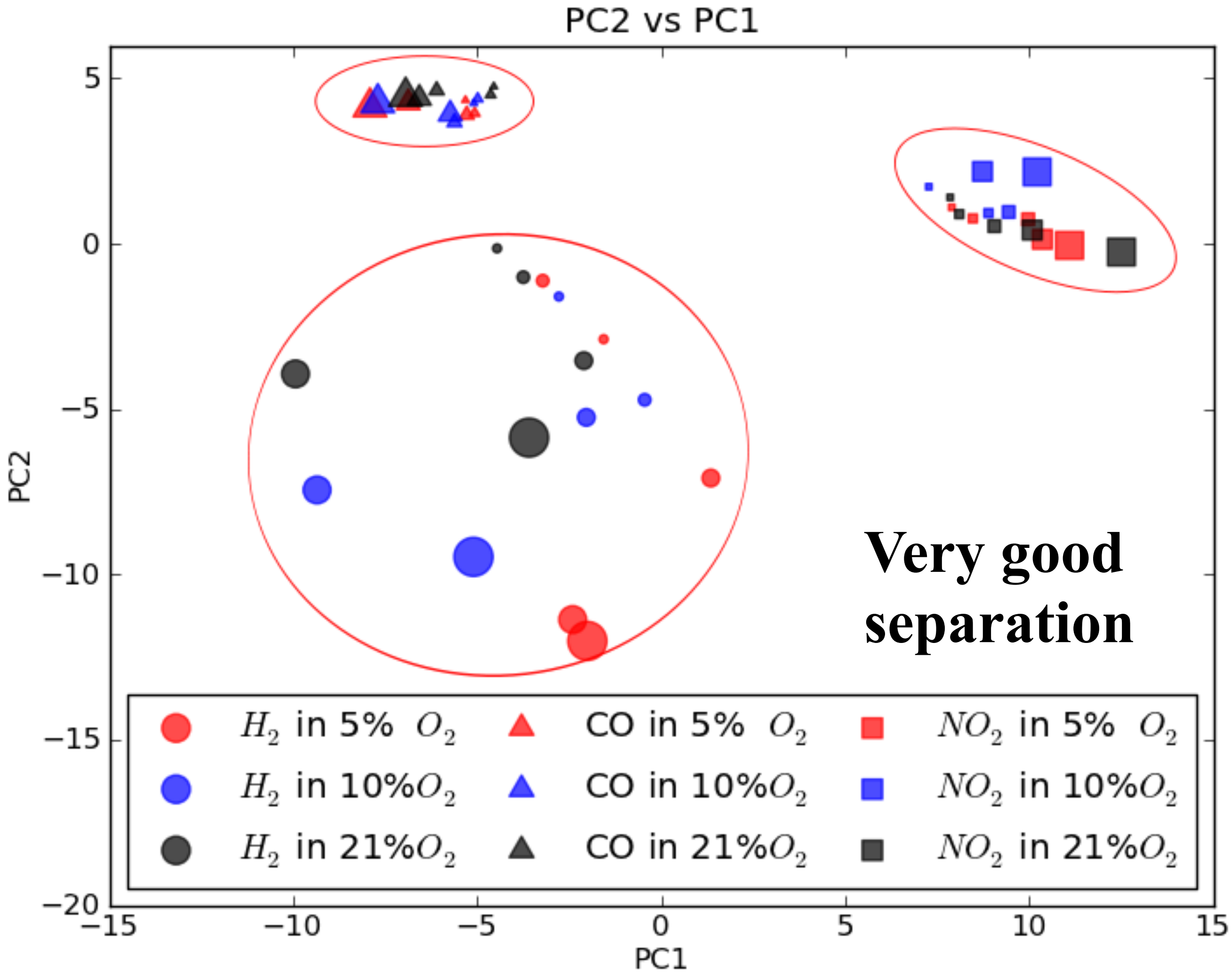


~390-1000nm = 630 *3 (sample #)

45 Observations:
5 concentrations
3 Analytes
3 O_2 backgrounds

Normalized and Mean Adjusted Data										
		[ppm]	388.105	388.717	389.329	389.941	390.553	391.165	391.777	39
H2	5% O2 Average	100	1.023027	-0.39367	-0.72012	0.00611	0.013789	-0.33971	0.490287	-0.4
		500	0.20441	0.056239	0.175303	-0.2122	-0.15136	0.090032	-0.42564	0.34
		1000	0.056563	0.093036	0.469755	-0.01796	0.179228	0.106737	0.026401	-0
		5000	0.73957	0.341386	-0.36616	0.173942	0.444829	-0.51202	0.002421	0.06
		10000	0.22457	-0.25529	0.099226	-0.28148	0.041378	0.326373	0.459625	0.30
H2	9.83% O2 Average	100	-0.51814	0.174142	0.399276	0.522277	0.369046	-0.09579	0.026065	-0.5

PCA Analysis of Sensor Array Data

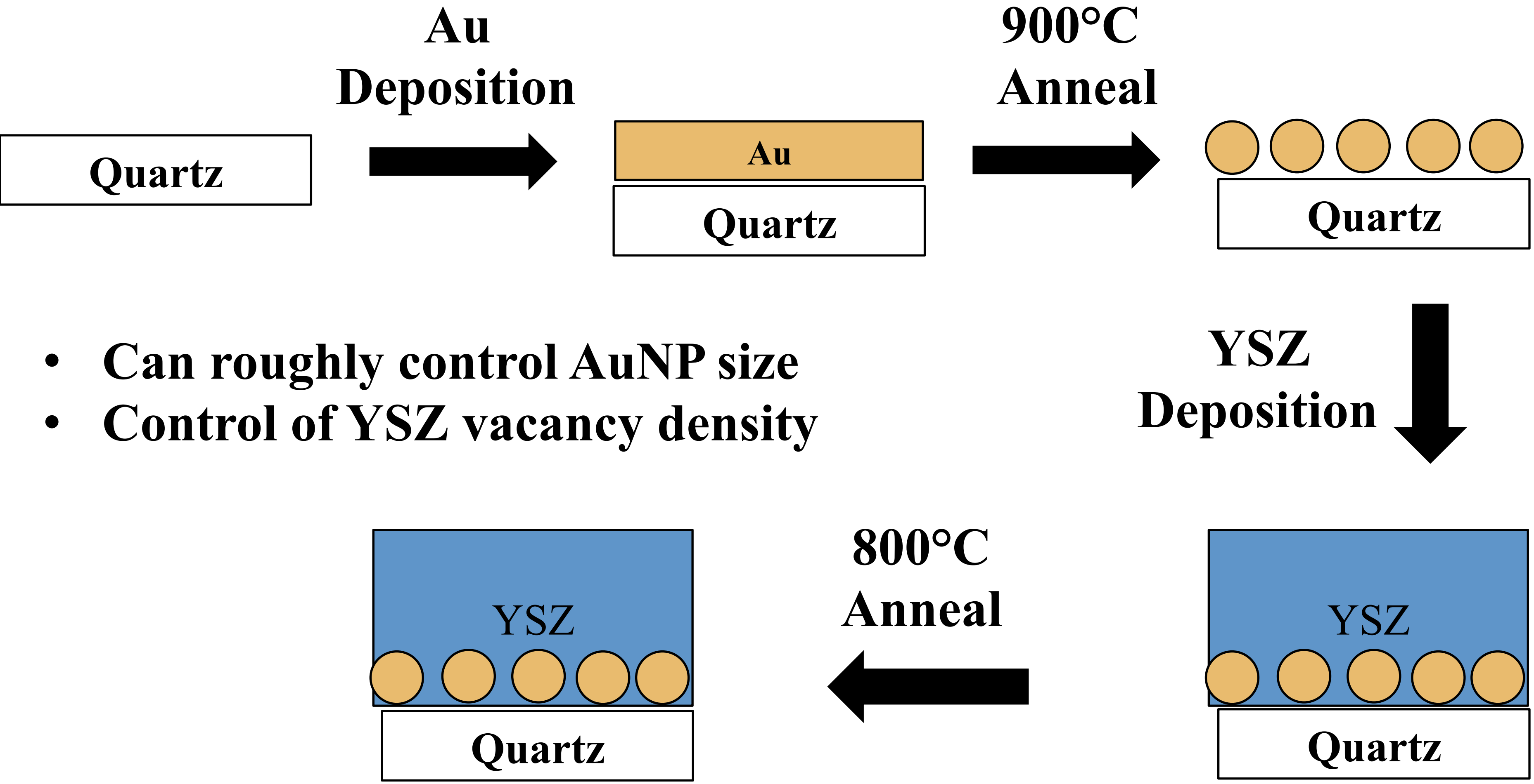


- **630 variables x 3 array elements = 1890 variables**
- **45 observables (5 gas concentrations, 3 target gases & 3 [O_2]**
- **~175 wavelengths used as inputs from the spectra**

N. A. Joy, P. H. Rogers, M. I. Nandasiri, S. Thevuthasan, M. A. Carpenter, *Plasmonic Based Sensing Using an Array of Au-Metal Oxide Thin Films*, Analytical Chemistry, **84**, 10437, (2012)

Selectivity through material control: Modifications to Au and YSZ properties

Layer by Layer Deposition Process:

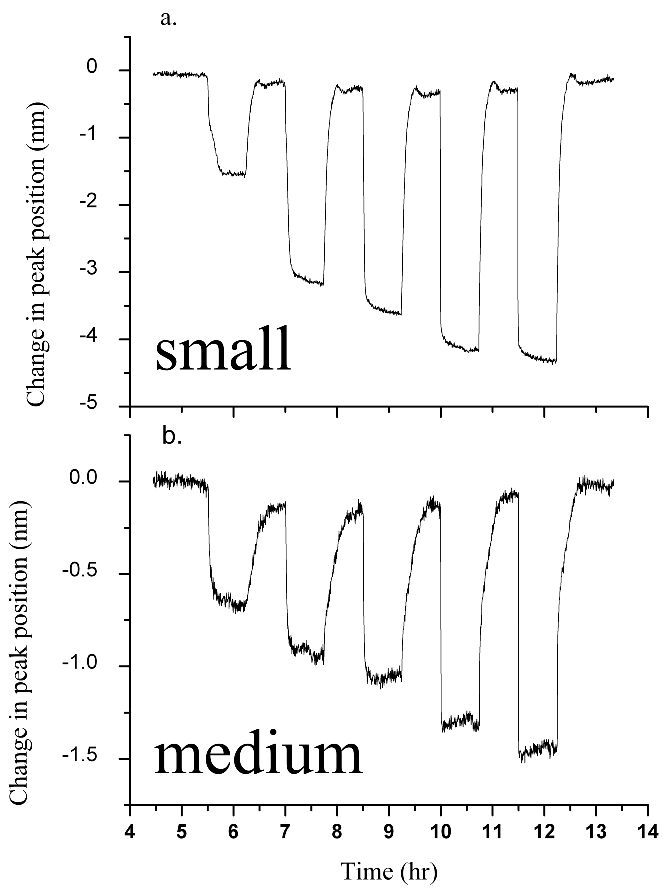


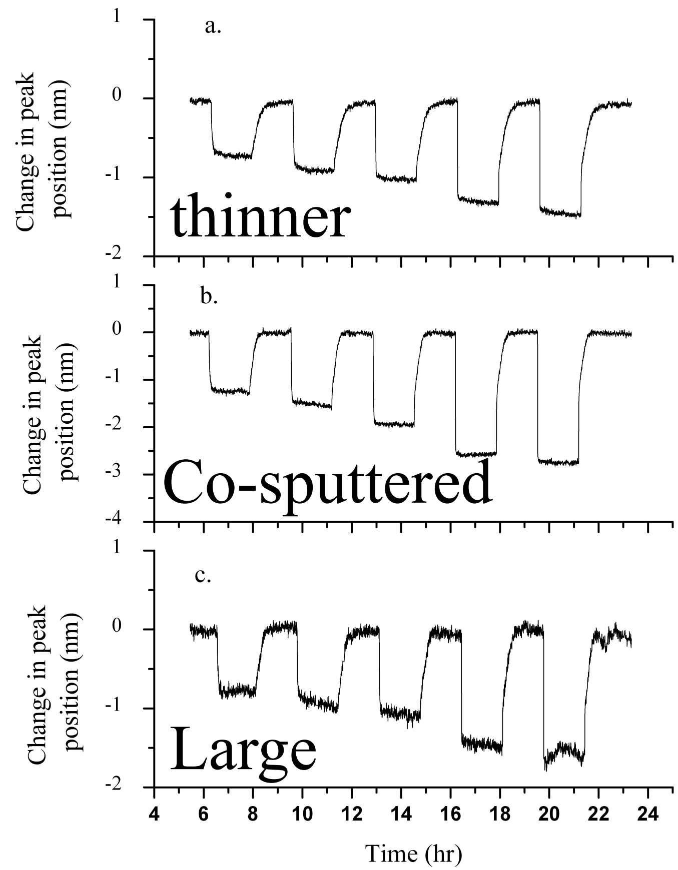
- Can roughly control AuNP size
- Control of YSZ vacancy density

	1.5 nm Au-20nm YSZ Cap	3nm Au-20nm YSZ Cap	3nm Au-5nm YSZ Cap	3nm Au-10nm YSZ Cap
Mean Diameter (nm)	57+/-16 **Thin***	48+/-14 **Small**	64+/-23 **Medium**	125+/-48 **Large***

Selectivity through material control: Modifications to Au and YSZ properties

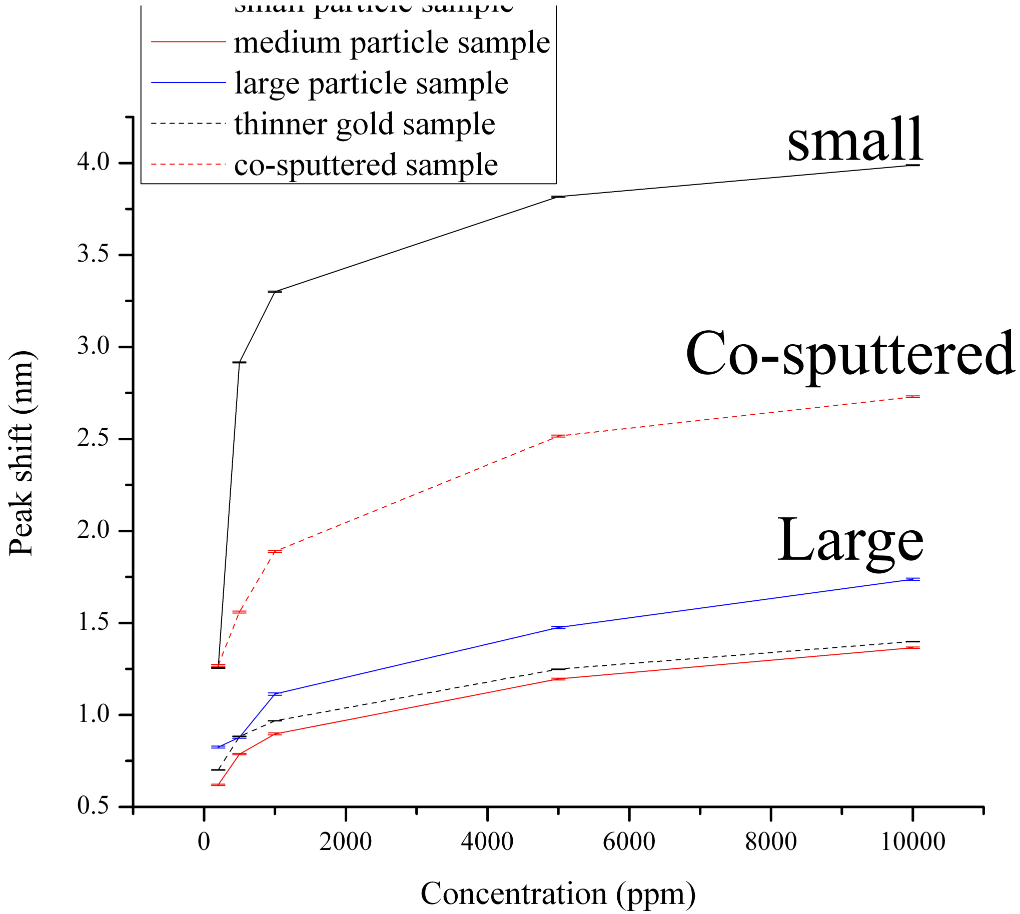
200, 500, 1000, 5000, 10000 ppm H_2 in air, 500°C





G. Dharmalingam, N. A. Joy, B. Grisafe, M. A. Carpenter, *Plasmonic Based Detection of H_2 and CO: Discrimination Between Reducing Gases Facilitated by Material Control*, Beilstein Journal of Nanotechnology, **3**, 712 (2012)

Selectivity through material control: Modifications to Au and YSZ properties



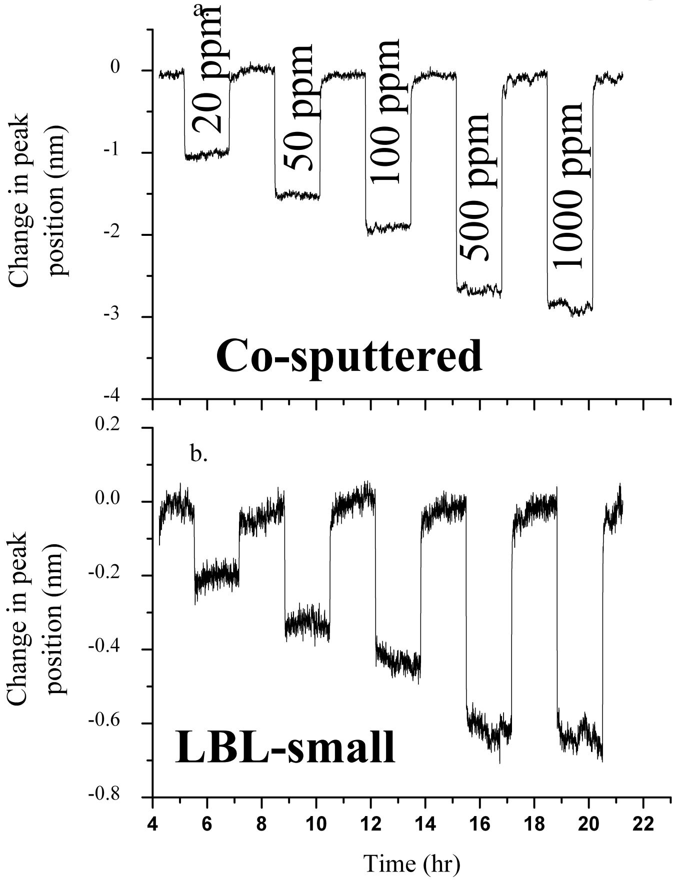
H_2 Sensing Character depends on YSZ

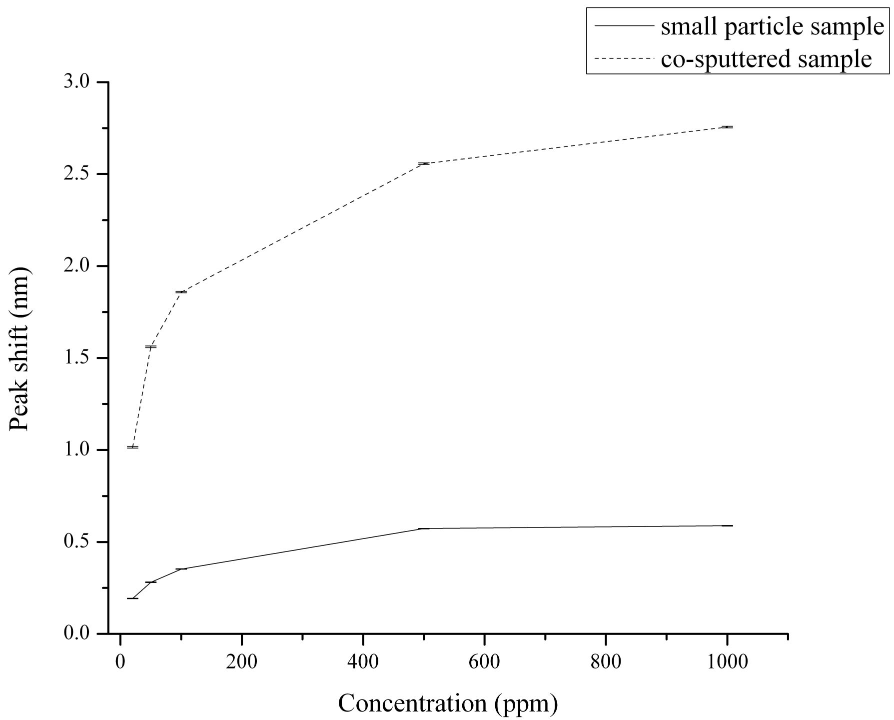
- Observed trends scale with estimated YSZ vacancy density of films

	1.5 nm Au-20nm YSZ Cap	3nm Au-20nm YSZ Cap	3nm Au-5nm YSZ Cap	3nm Au-10nm YSZ Cap
YSZ Vacancy(x10^{15} cm^{-2})	8 **(Thin*)**	8 **(Small)**	2 **(Medium)**	4 **(Large*)**

CO Comparison: Layer-by-layer(small) vs. co-sputtered sample

@500^{o}C in air



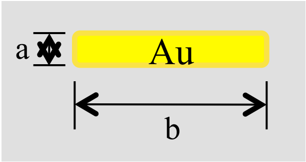


Co-sputtered sample better by a factor of ~4 than layer by layer

-these samples have an average particle size of ~20nm, smaller than LBL sample

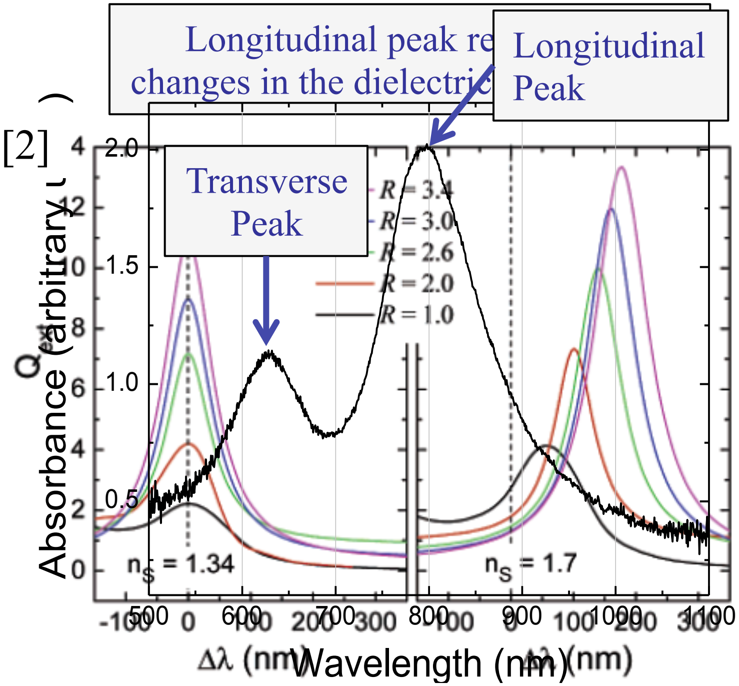
Why Au Nanorods?

1. Two SPR absorbance peaks
2. Tunable longitudinal peak position
3. Catalysis by gold nanoparticles is size dependent[1]
4. Sensitivity is shape dependent[2]



aspect ratio = b/a

[2]

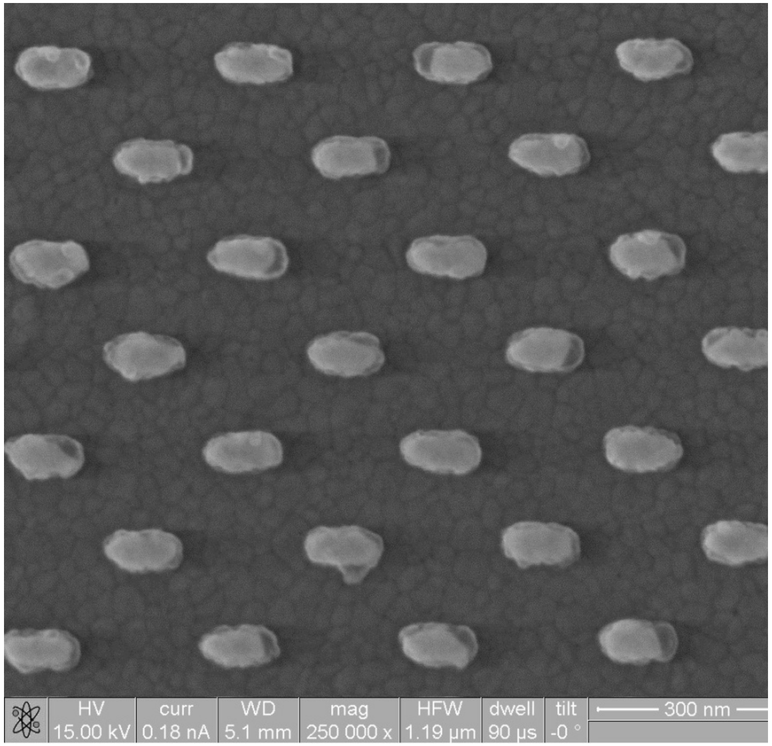


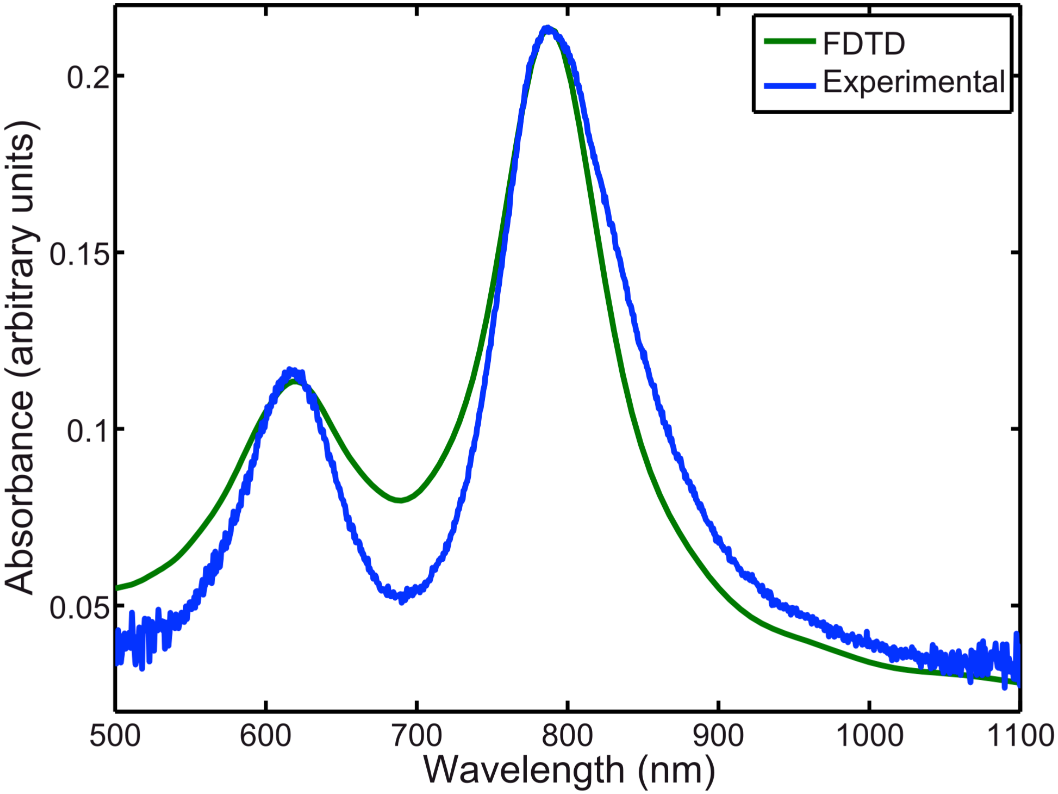
Challenges:

1. Thermal Stability
2. Show sensing response from both peaks

[1] M. Haruta, "Size- and support-dependency in the catalysis of gold," *Catalysis Today*, vol. 36, no. 1, pp. 153–166, Apr. 1997.
[2] K.-S. Lee and M. A. El-Sayed, "Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition," *The Journal of Physical Chemistry B*, vol. 110, no. 39, pp. 19220-19225, Oct. 2006.

Summary of the Sample Used for Sensing Tests



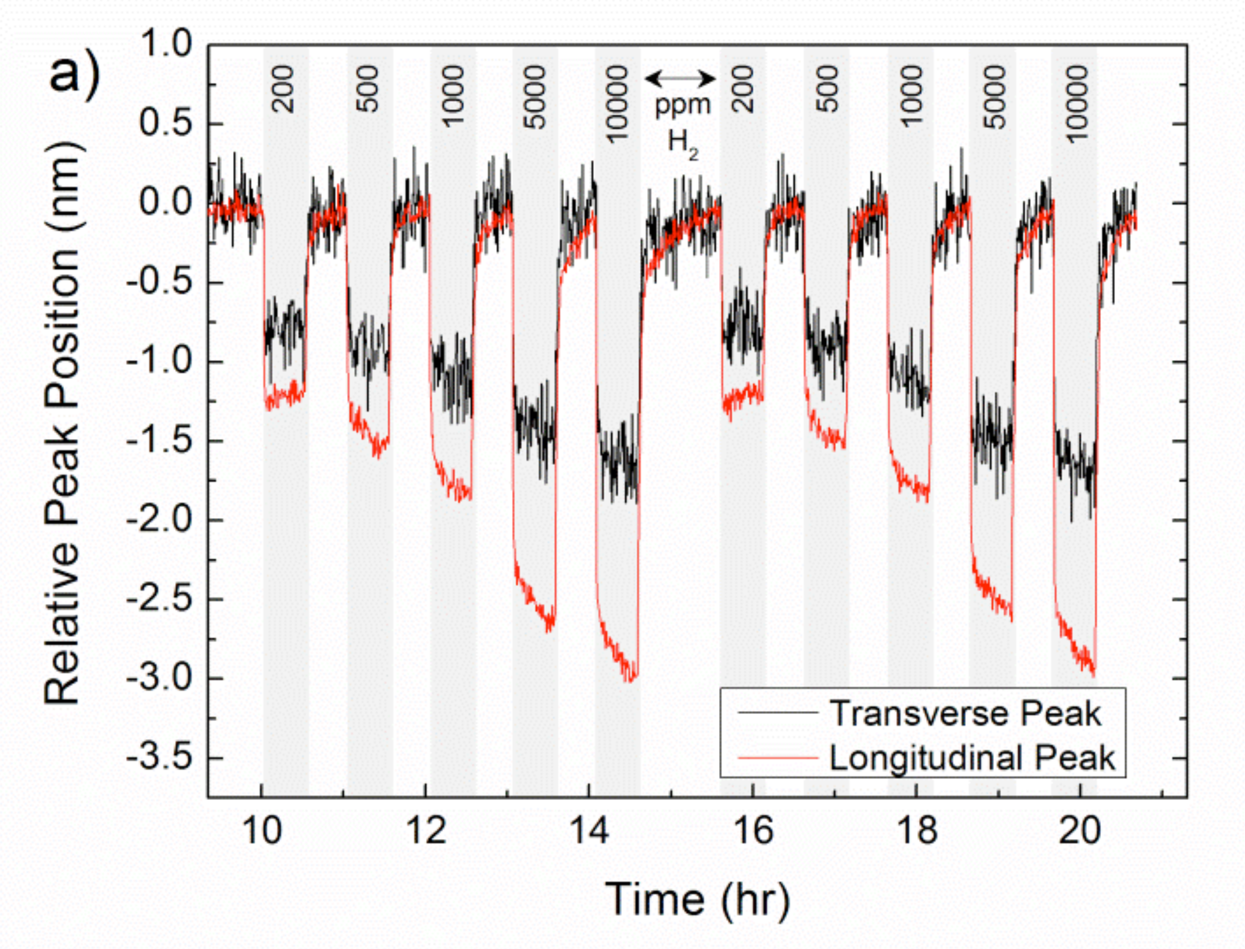


- 44 x 130 nm nominal dimensions
- 15 nm YSZ capping layer
- Annealed up to 600°C for 6 hours

- 500°C, air background
- H_2, NO_2, and CO sensing tests
- Both peak positions monitored

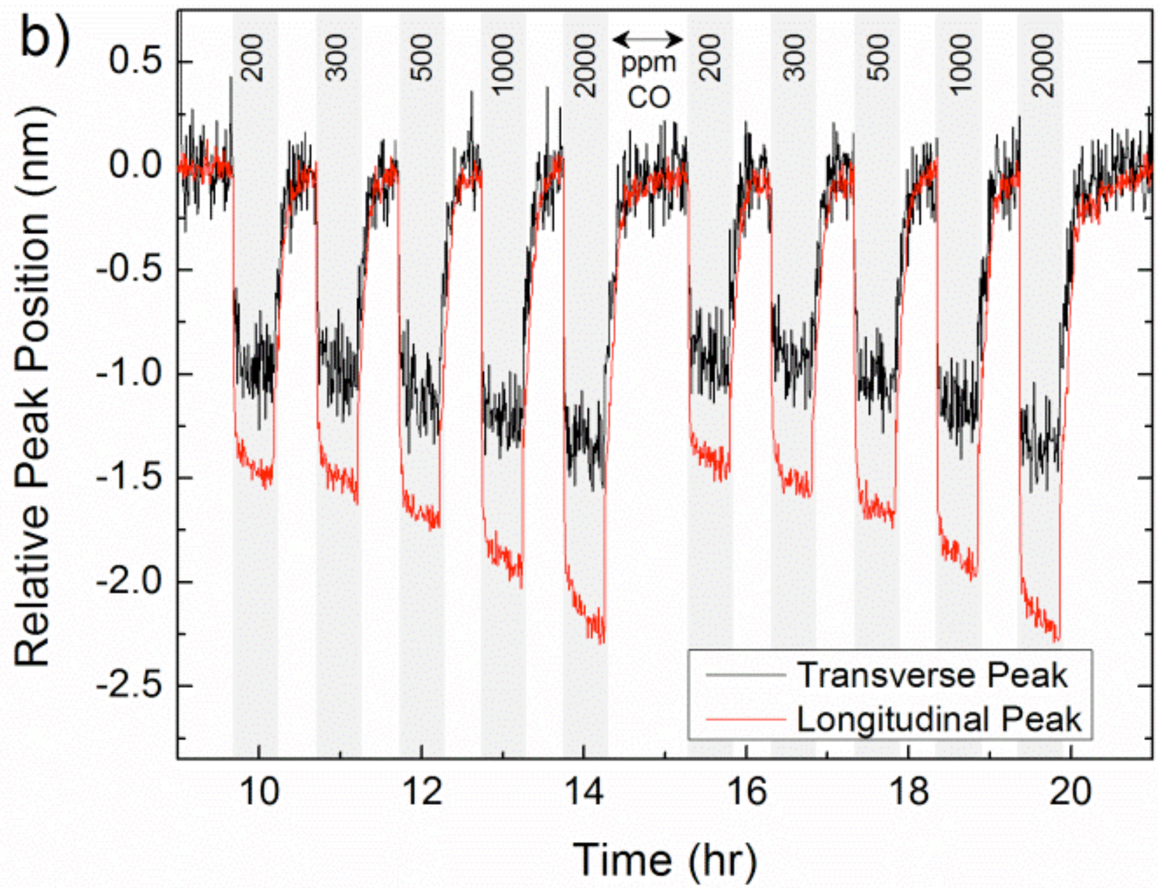
N. A. Joy, B. K. Janiszewski, S. Novak, T. W. Johnson. S-H Oh, A. Raghunathan, J. Hartley, M. A. Carpenter, *Thermal Stability of Gold Nanorods for High Temperature Plasmonic Sensing*, J. Phys. Chem. C, **117**, 11718 (2013)

H_2 Exposure Plots at 500°C in Air



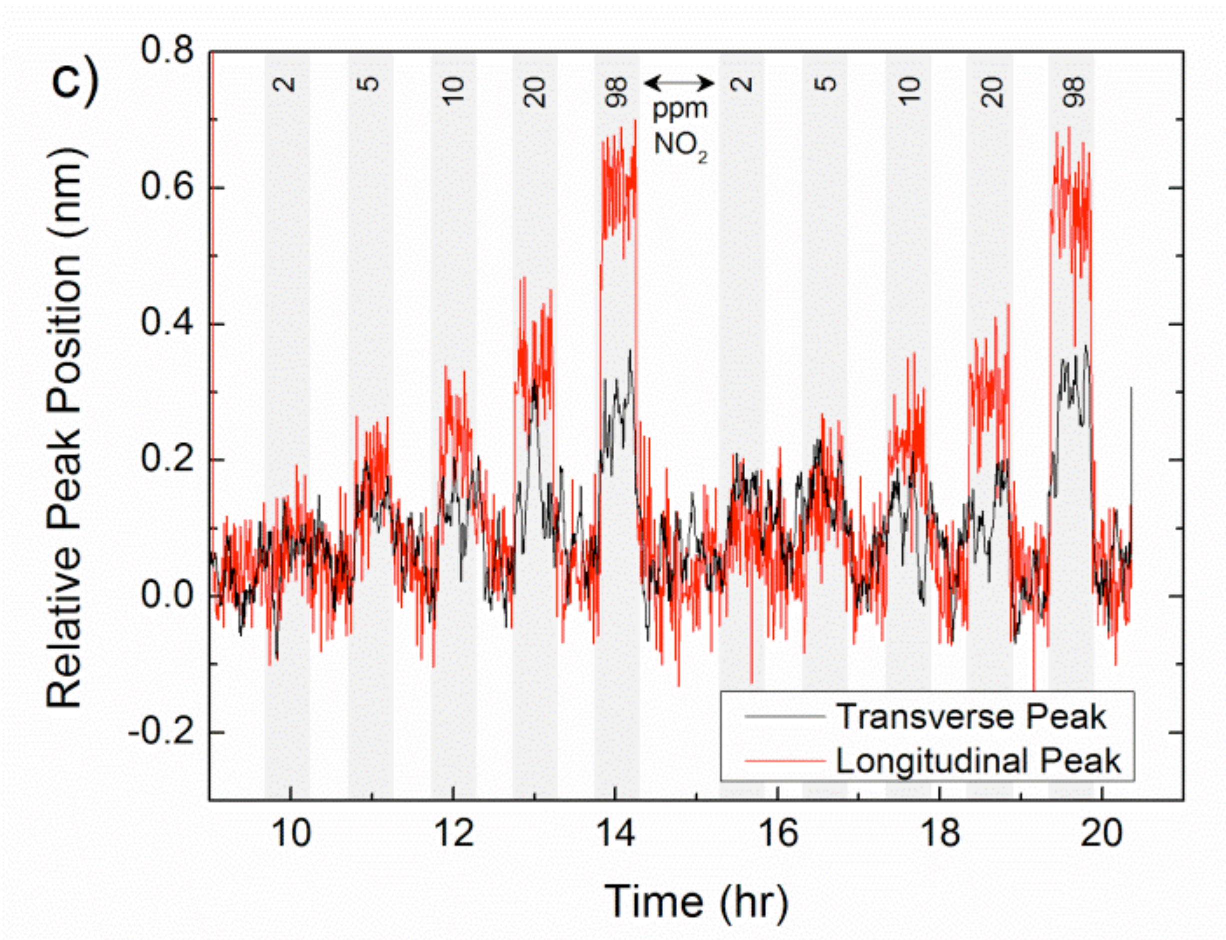
Nanorods: CO sensing data

500^{o}C in air, 44x130nm rods

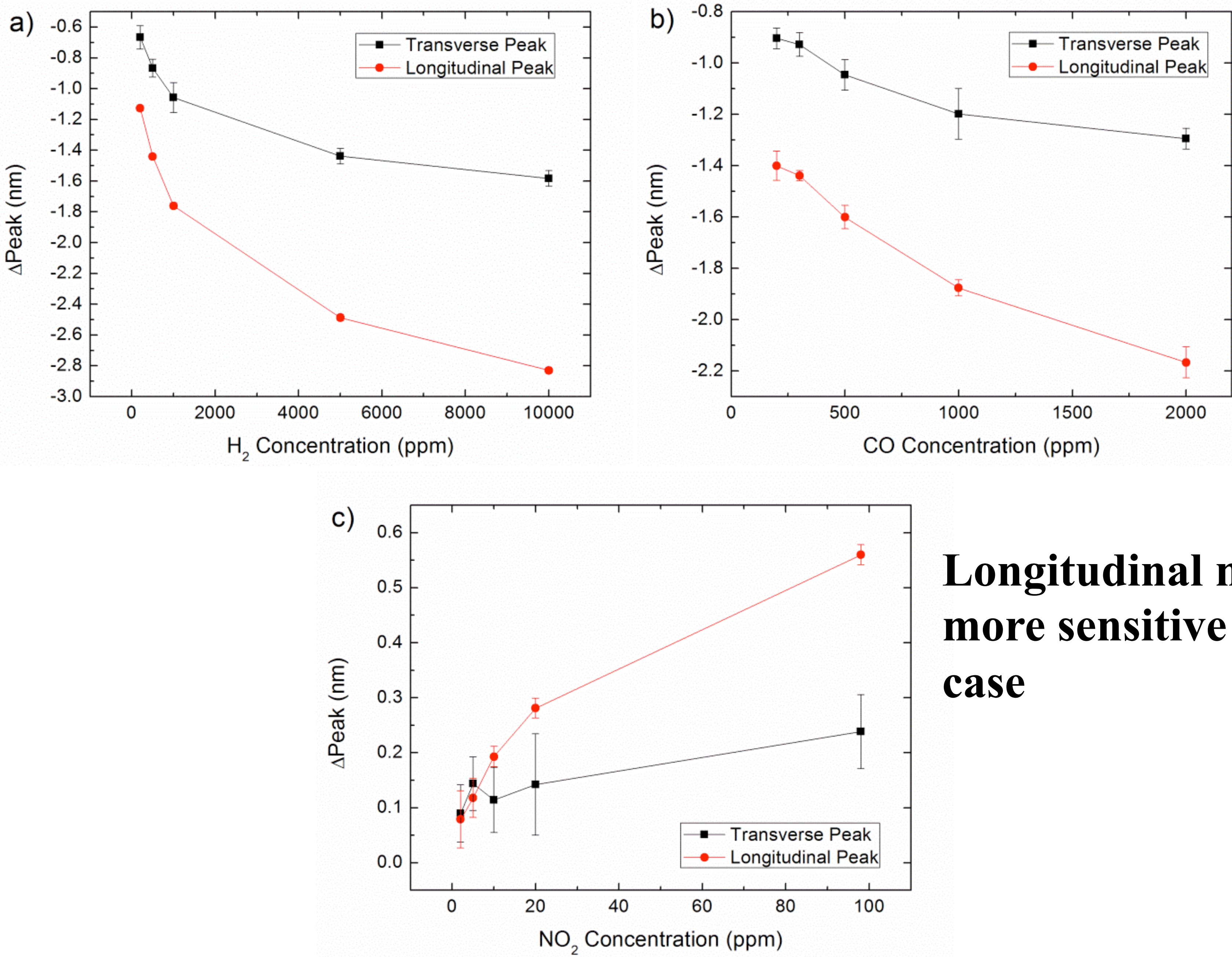


Nanorods: NO_2 Sensing Data

500^{o}C in air, 44x130nm rods

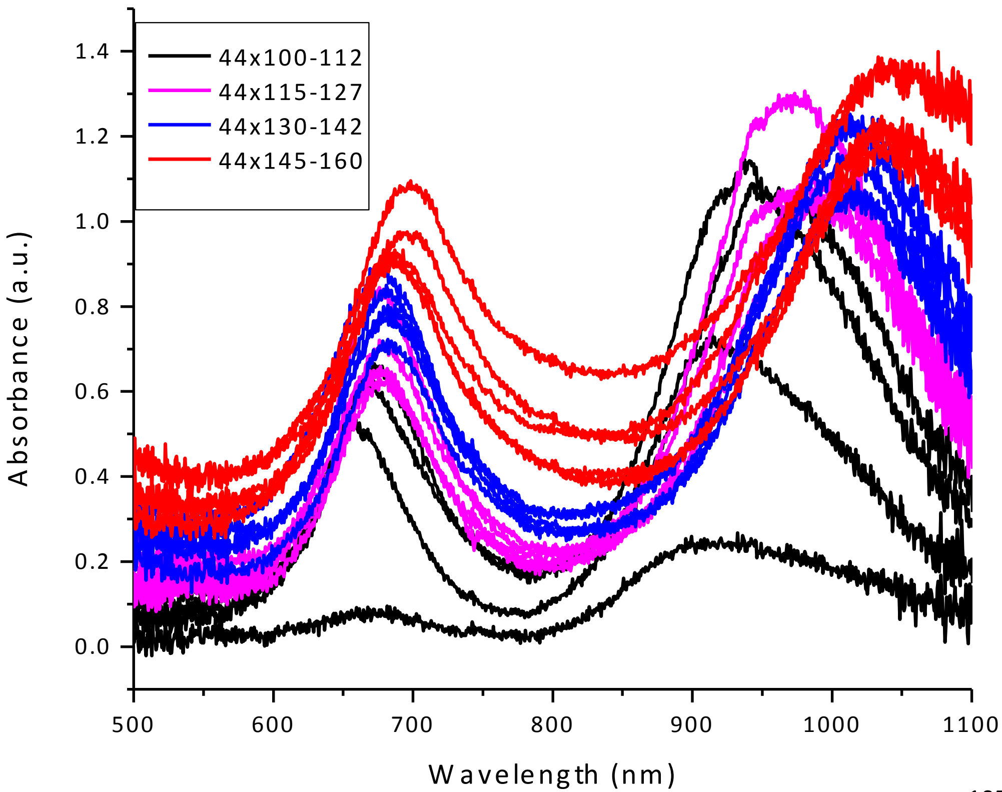


H_2 , CO and NO_2 calibration curves for 44x130nm nanorod



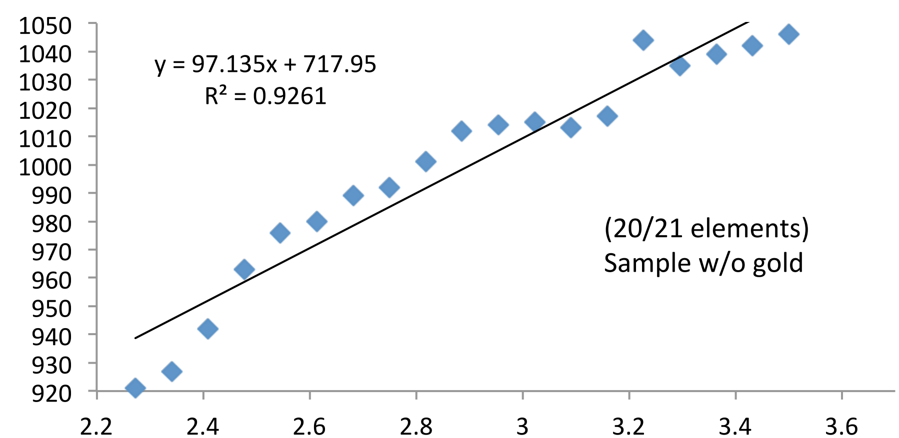
Longitudinal mode is more sensitive in each case

Sensor Testing: Large Arrays of Nanorods



Linear relationship between longitudinal mode and aspect ratio

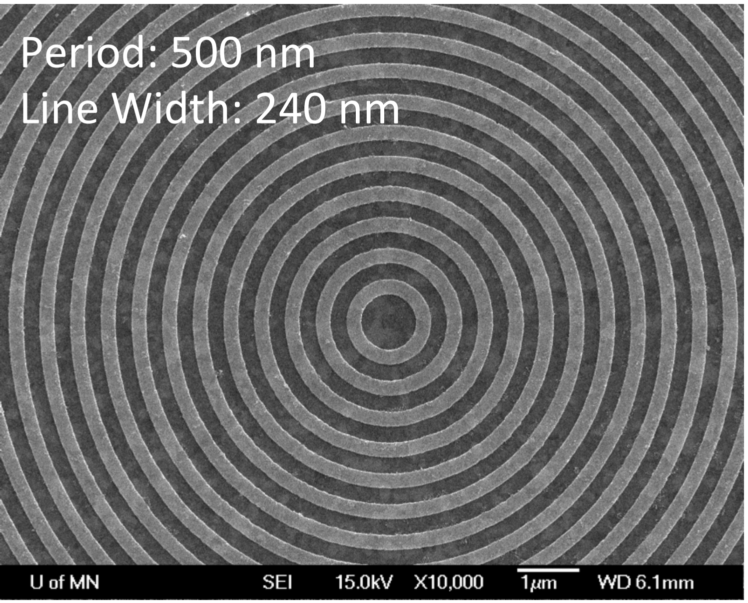
Longitudinal Peak wavelength vs. Aspect Ratio

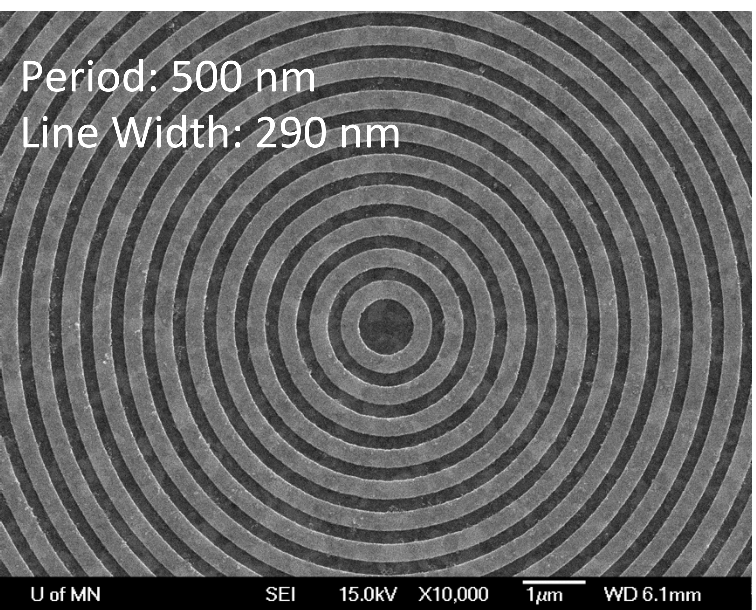


As aspect ratio increases both radial and longitudinal modes redshift

Sensing tests on large arrays in progress

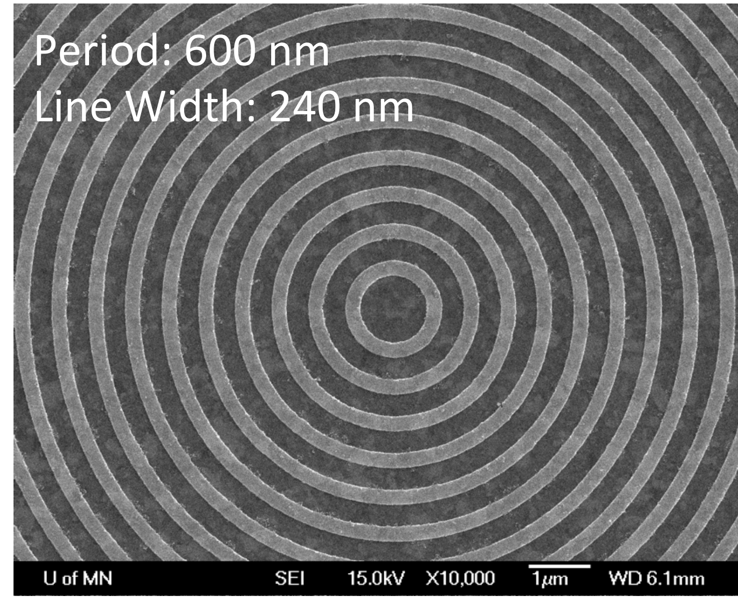
Varying the Bull's Eye Dimensions

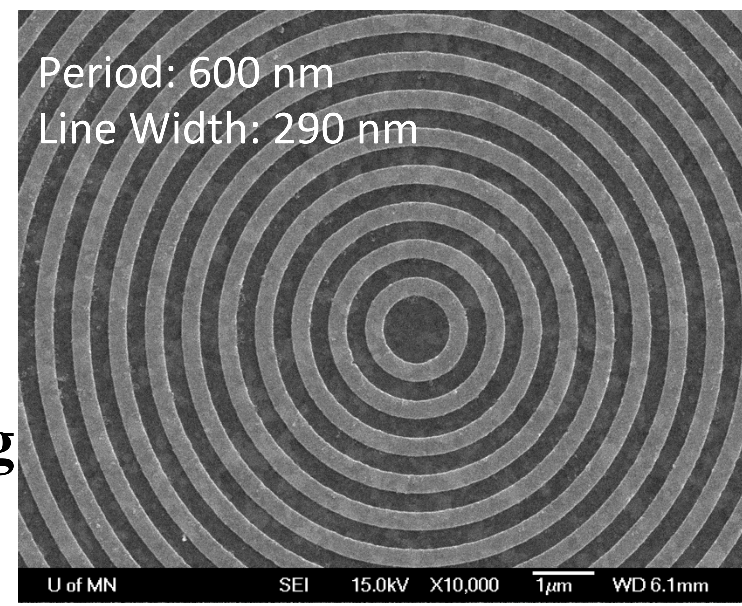




By changing the period and the line width of the grating the plasmonic spectra can be tuned to match that of the patterned nanorods

Thermal stability testing in progress

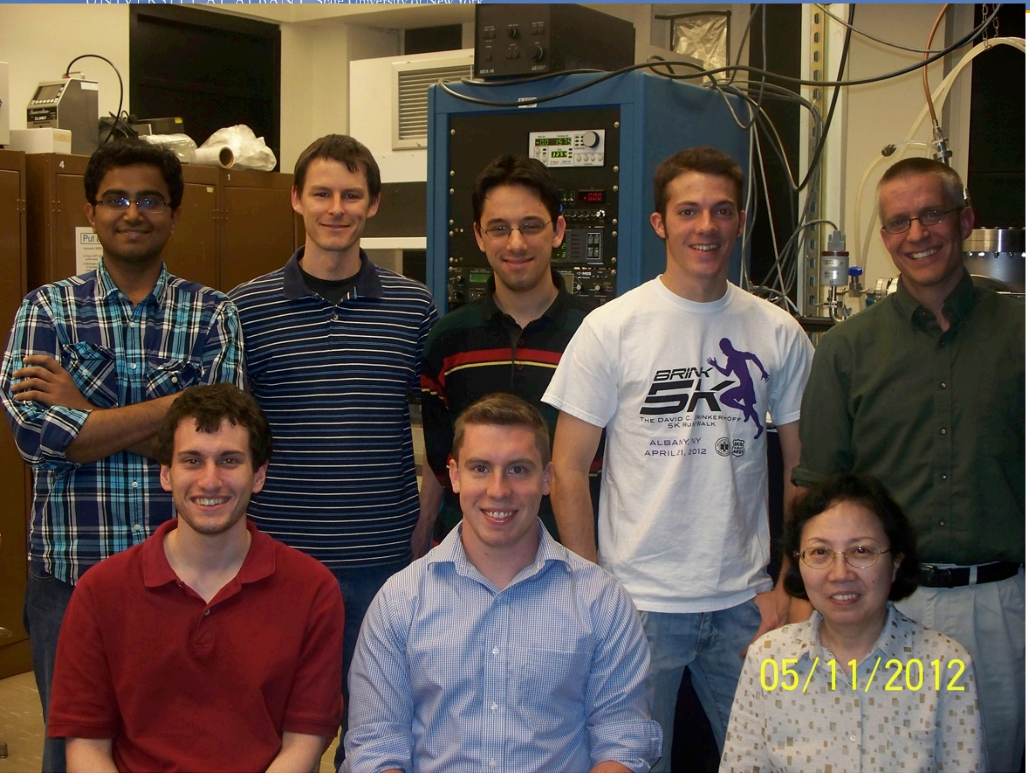




Summary and Future Work

- **Demonstrated selectivity enhancements through array analysis with PCA as well as materials optimization**
- **Developed ebeam lithography techniques for depositing patterns of Au-metal oxide nanoparticle arrays**
- **Demonstrated thermal stability and sensing characteristics of nanorod samples**
- **Sensor testing of large rod arrays in progress**
- **Bulls-eye design and development in progress**
- **Thermal stability optimization steps continuing**

Acknowledgements



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Ryan O'Connor(UG)

University of Minnesota

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Tim Johnson (Ph.D.)
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