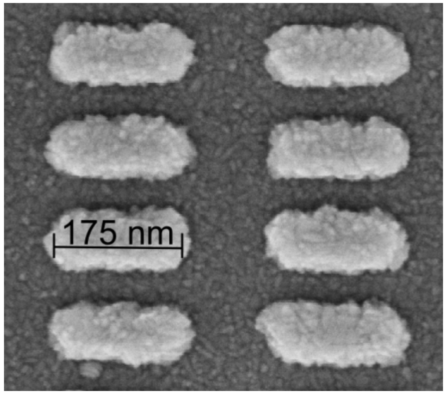
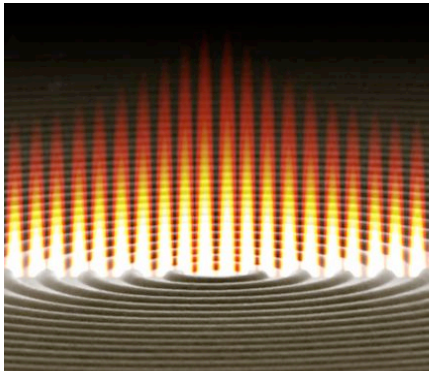


Carpenter Group, CNSE


Oh group, University of Minnesota

Heat-activated Plasmonic Chemical Sensors for Harsh Environments

Dr. Michael A. Carpenter
College of NanoScale Science and Engineering
Energy & Environmental Technology Applications Center
University at Albany – SUNY

Dr. Sang-Hyun Oh
Department of Electrical and Computer Engineering
University of Minnesota-Twin Cities

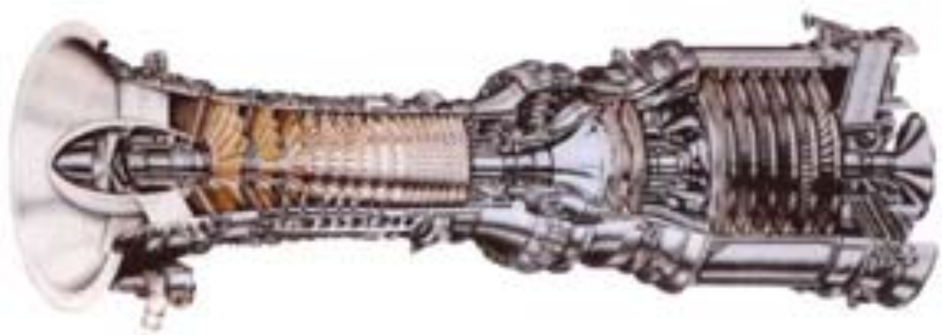
5/20/14

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

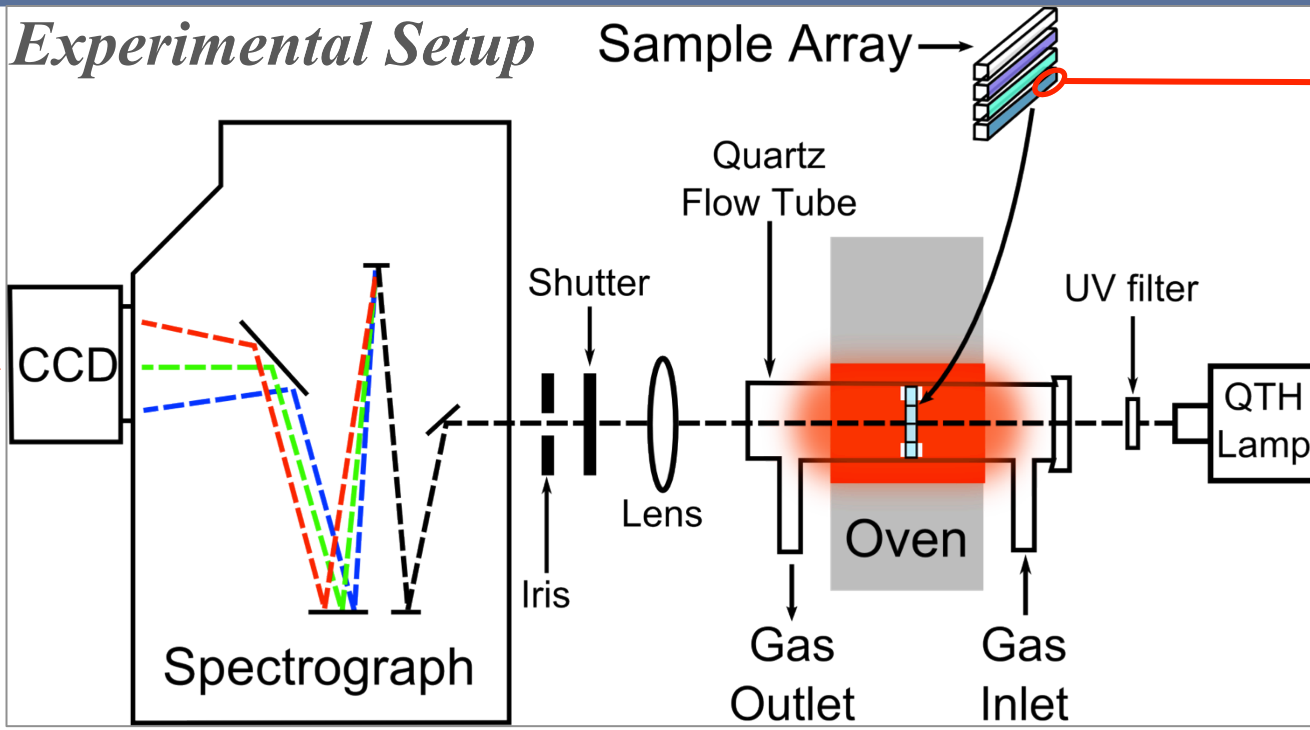


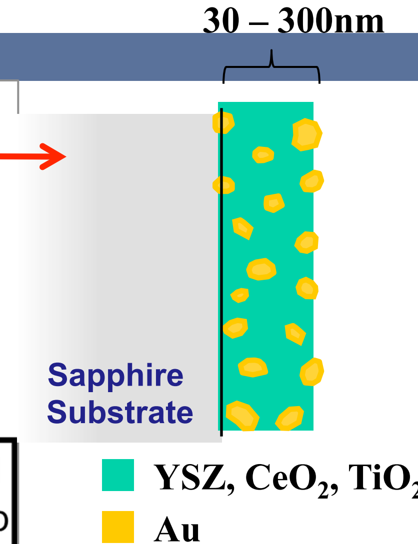
Goals of Research are Two-Fold

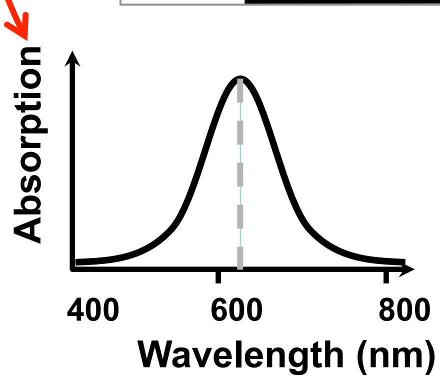
1. Develop prototype nanorod materials for use in next generation sensing devices
   - Sensitivity, reliability, selectivity
2. Design and develop bulls-eye energy harvesting structures

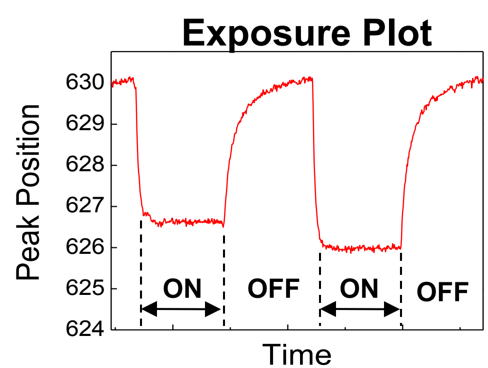
Why do we need energy harvesting?

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

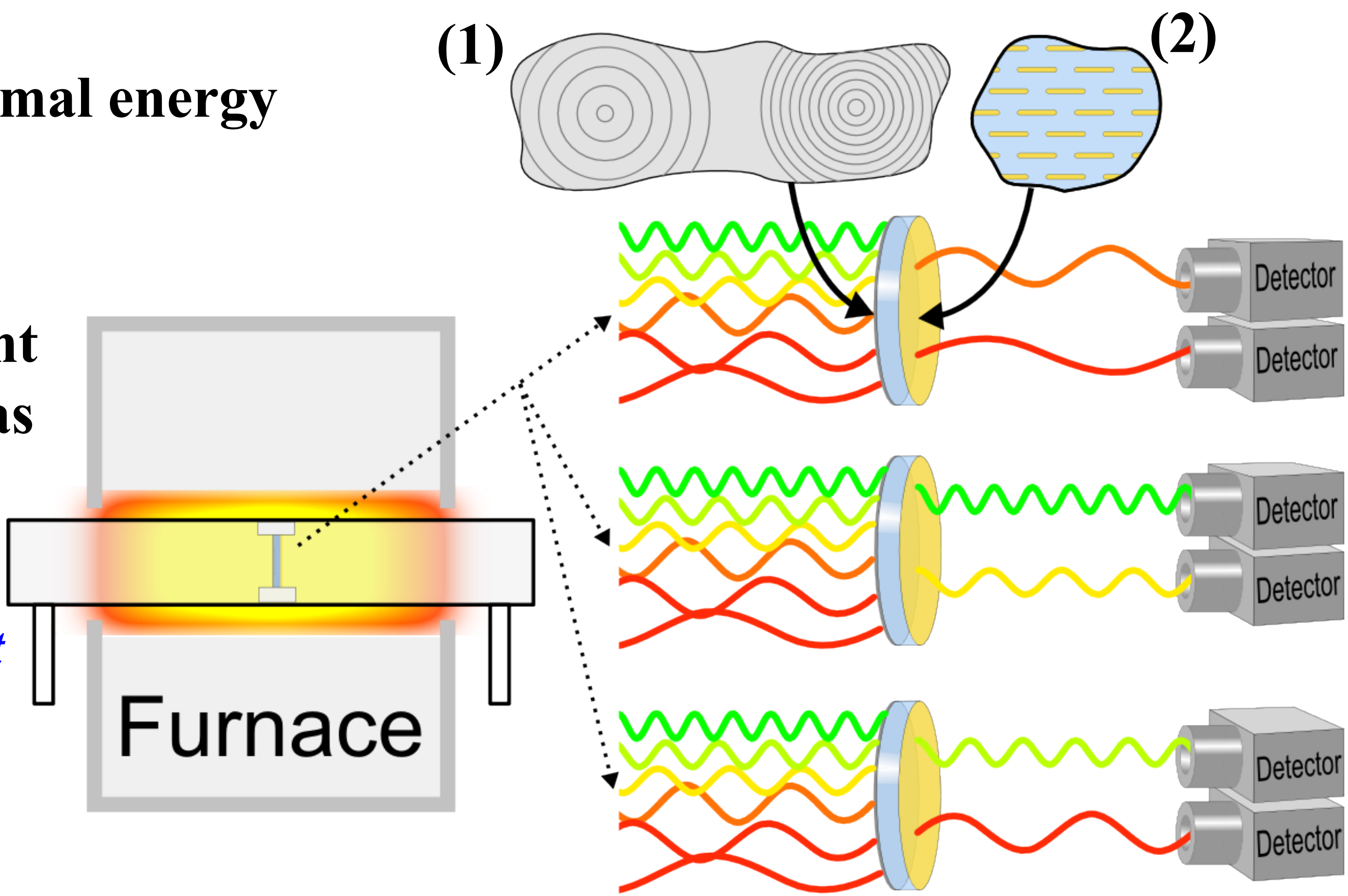
- Absorbs thermal energy
- Emits light

(2) Nanorods

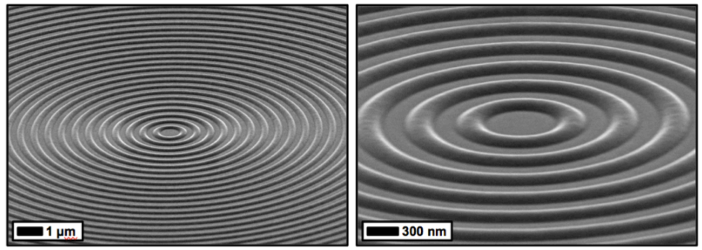
Transmitted light dependent on gas exposure

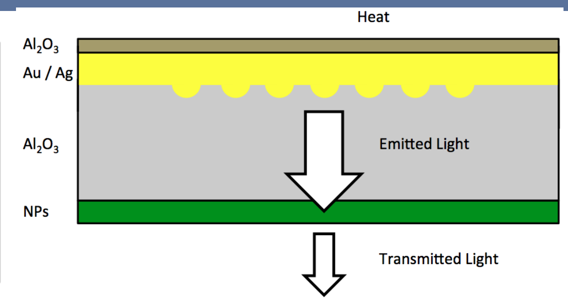
No external light source required

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

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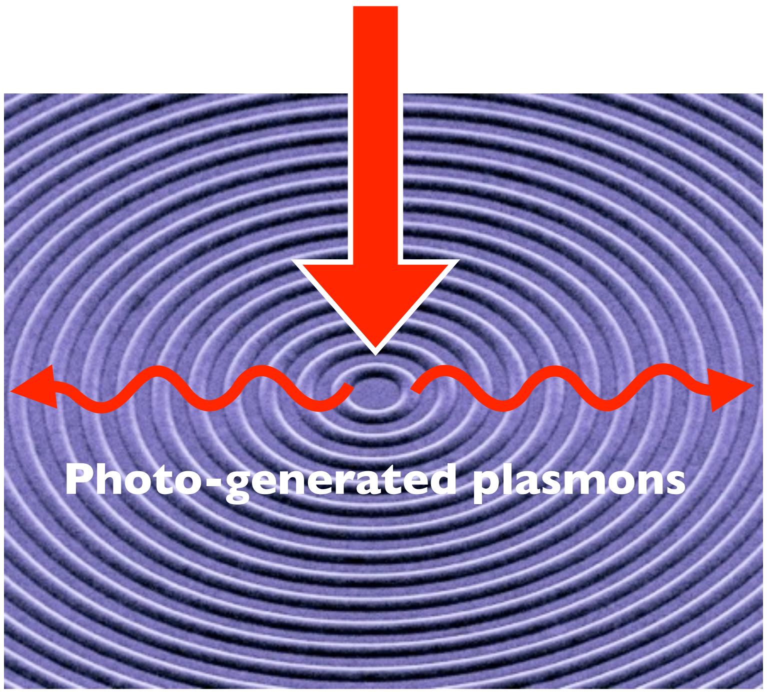
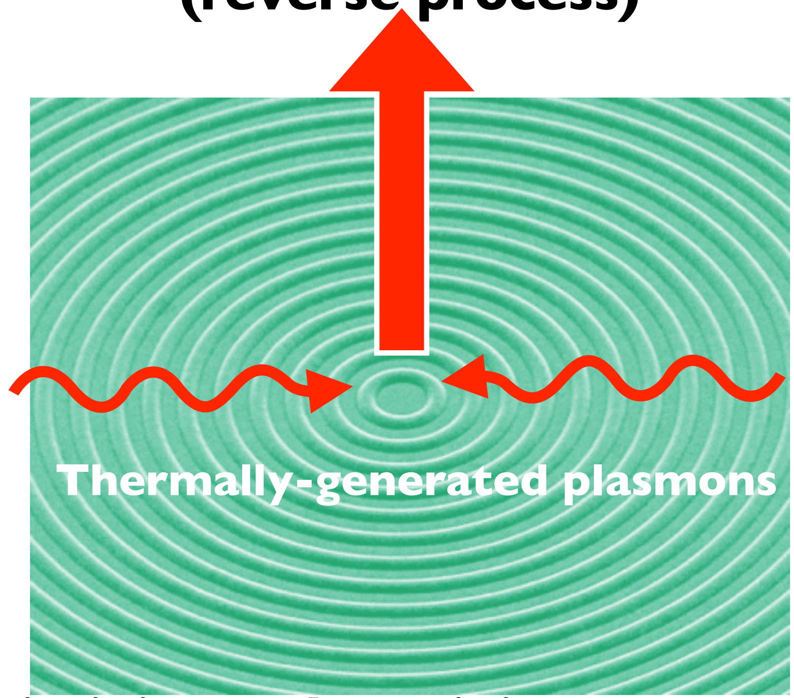
Bulls-eye Basics: Thermal Excitation of Plasmons

Light absorption



Thermal emission (reverse process)



- **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.**

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

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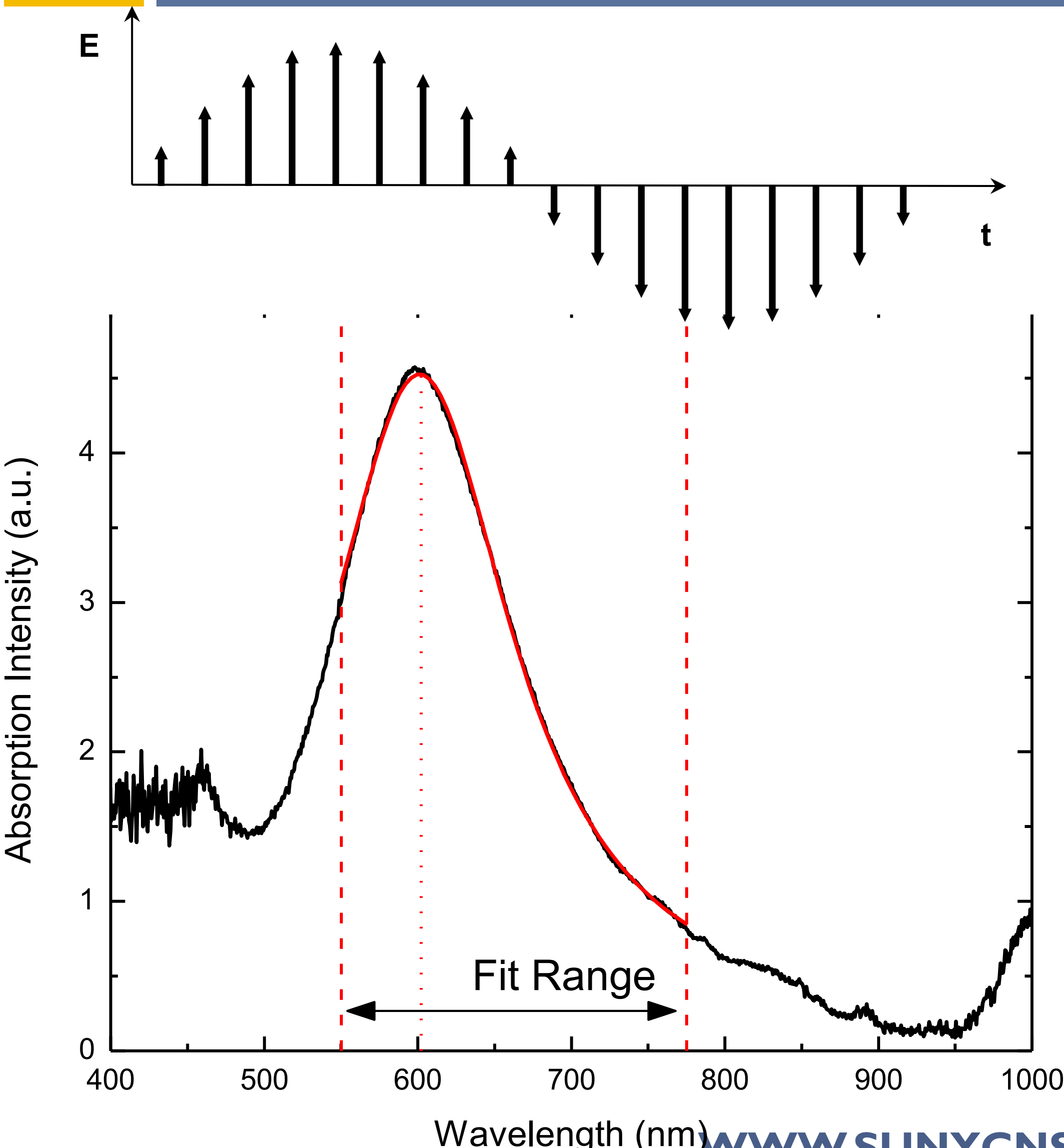
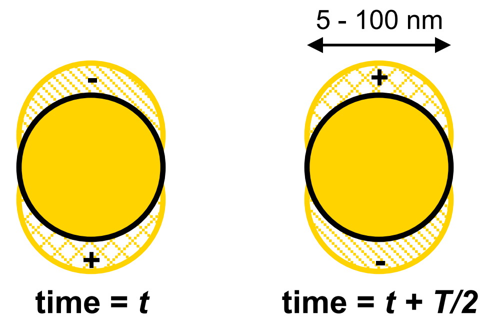
Background - Au Nanoparticles as Optical Beacons For Transduction Events





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

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

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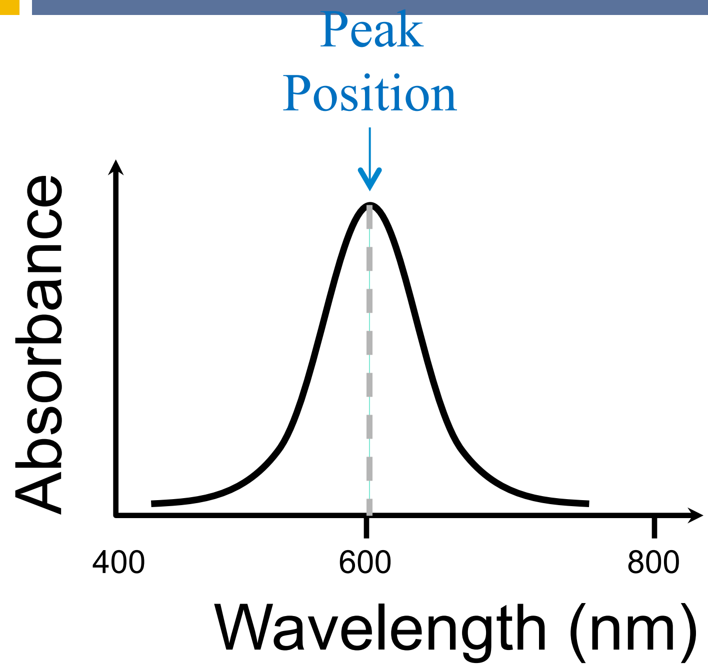
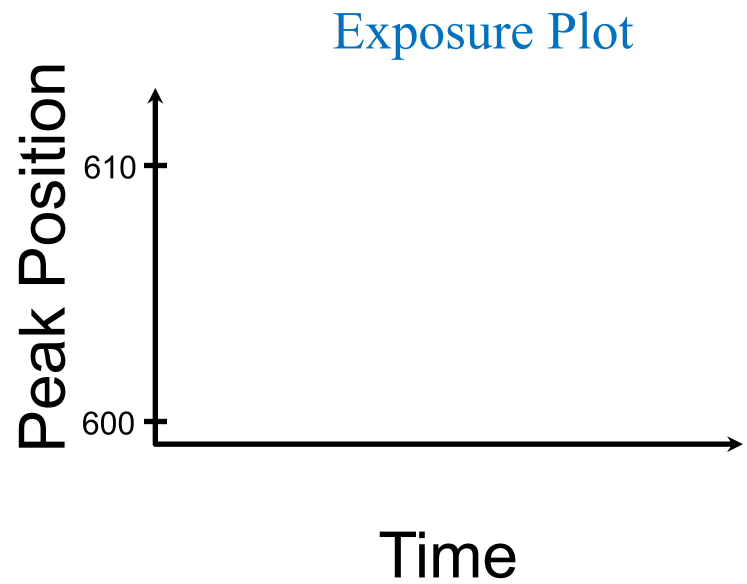
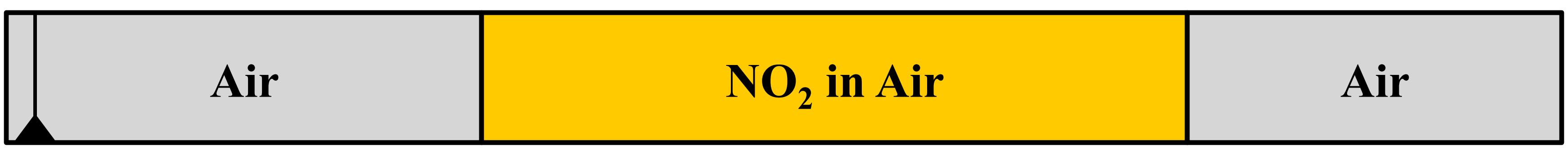
Example of Data Acquisition





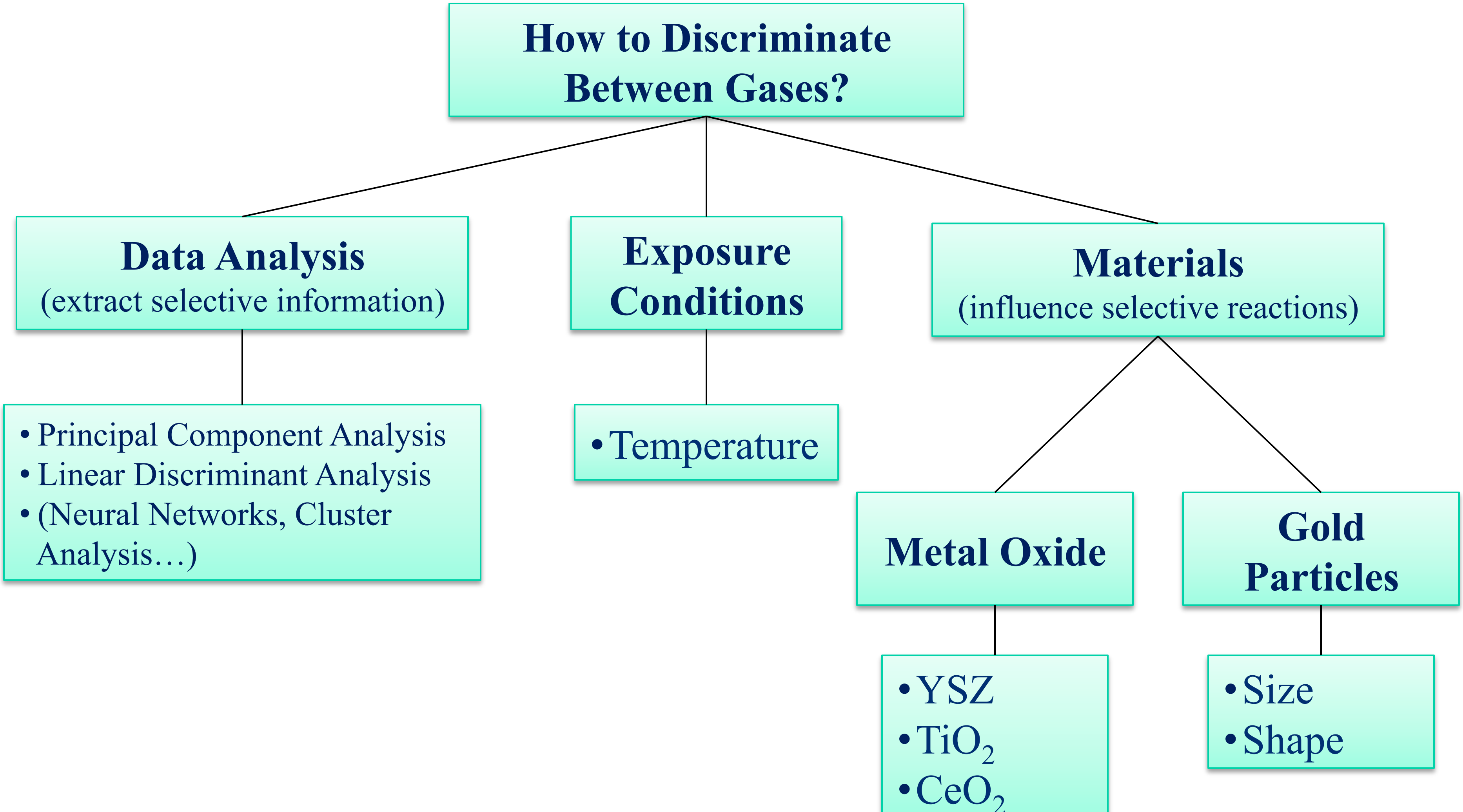


$$\Delta\Omega \propto \Delta\sqrt{\frac{N}{(1+2\varepsilon_m)}}$$

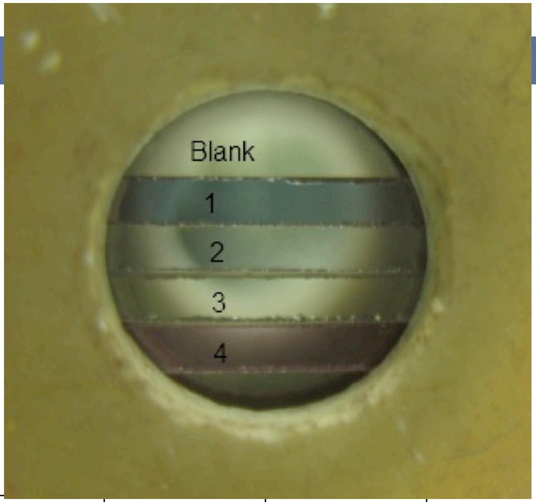
H_2, CO — Reducing

NO_2 — Oxidizing

Selectivity Challenge



Sensor Array Studies



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

- Ceria is 200nm thick
- 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**

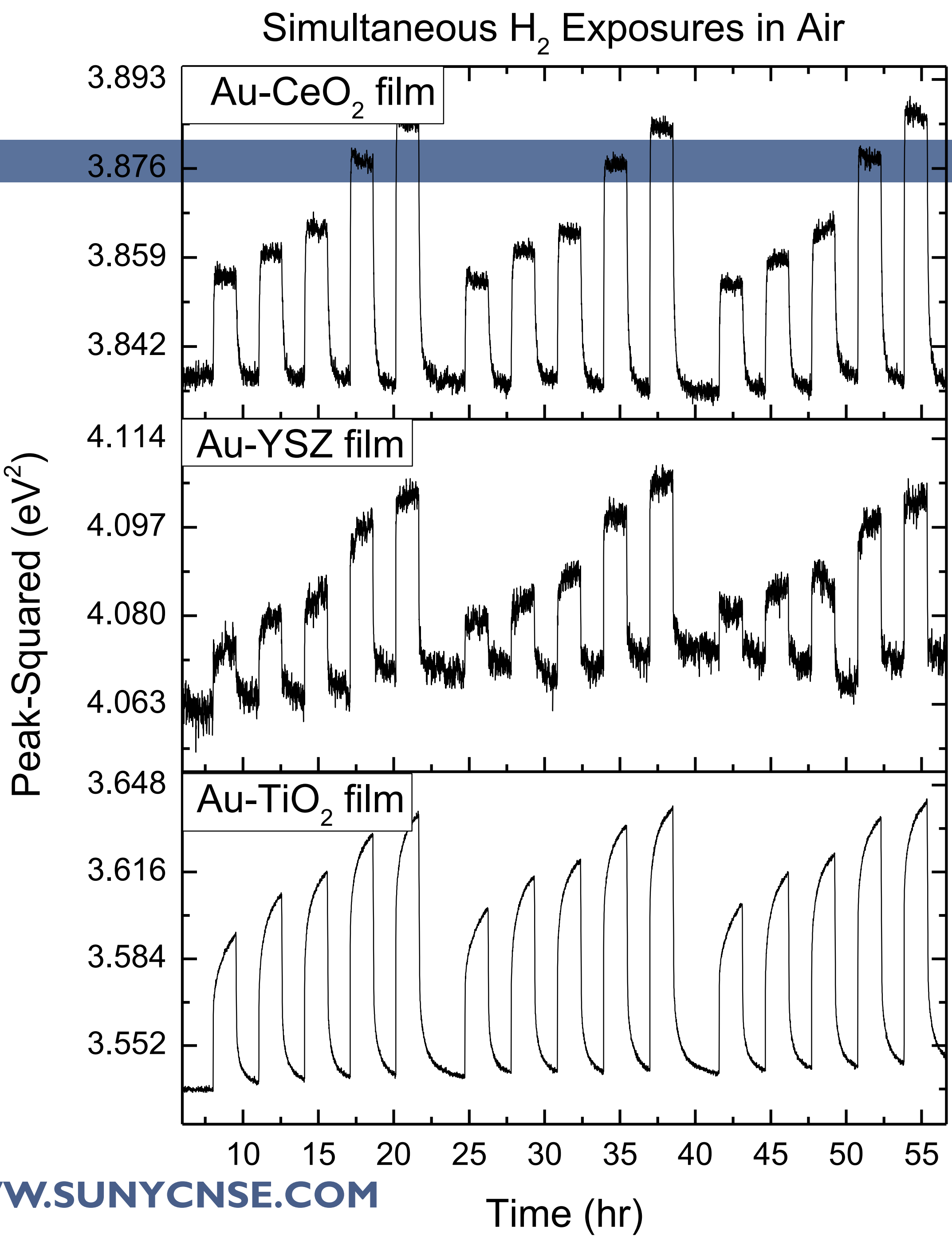
- ~30nm thick Au-TiO_2
- Au particle size ~25nm
- ~10 at.% Au

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	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

H_2 in Air @ 500°C



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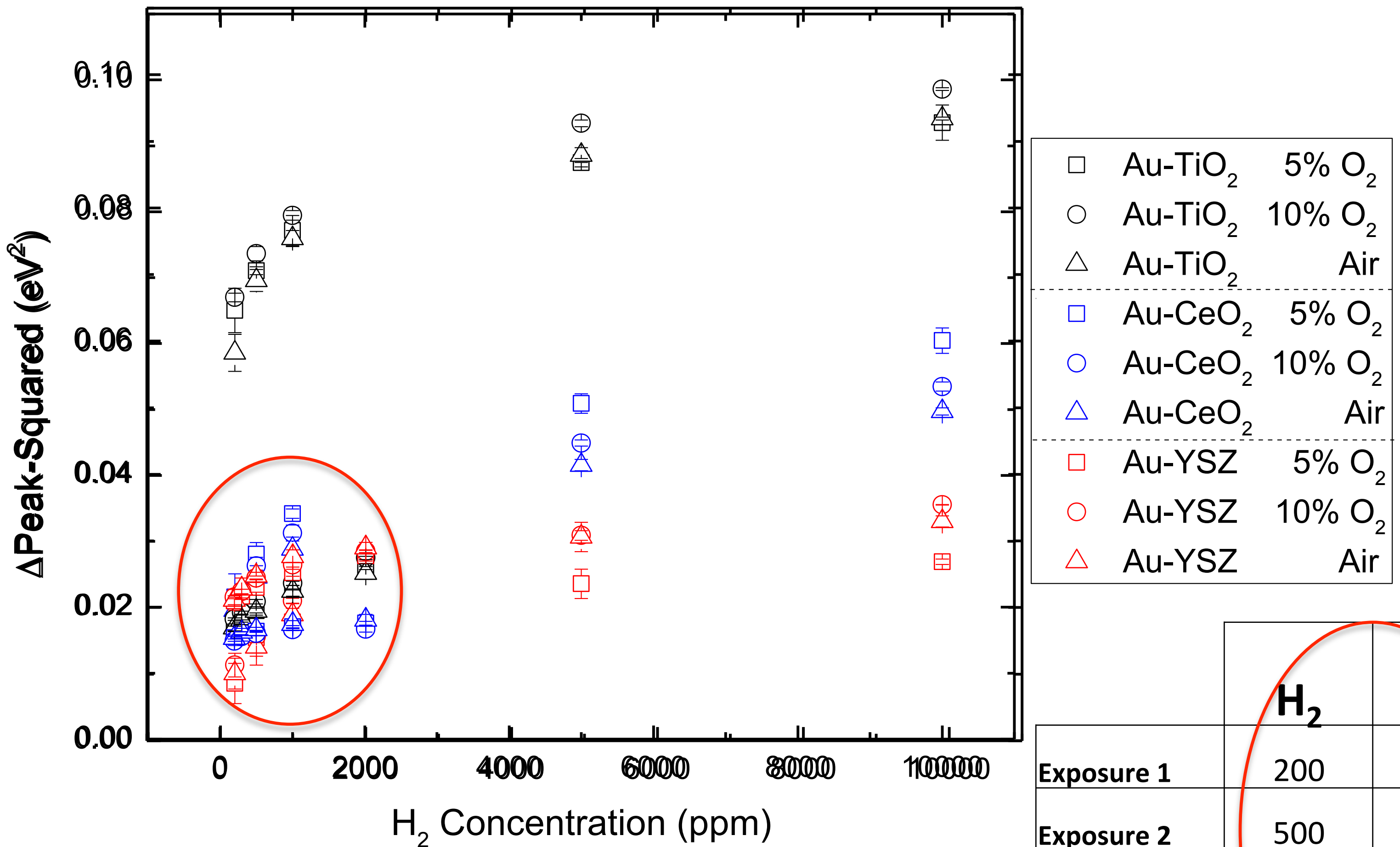
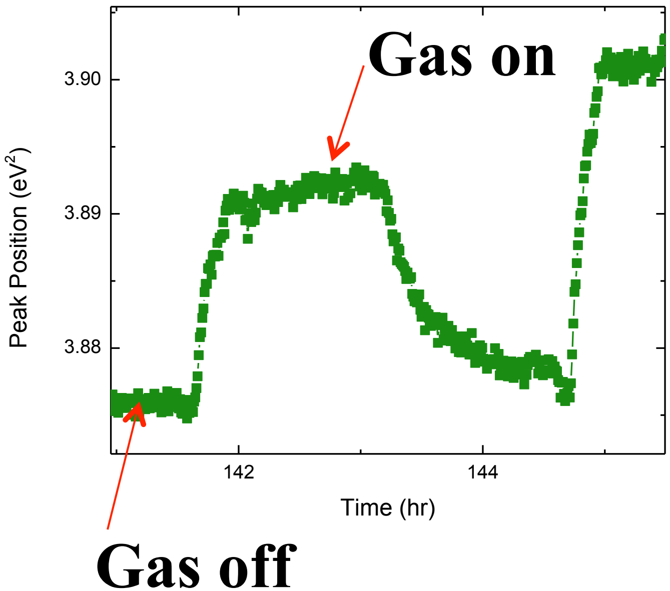
H_2 ΔPeak vs Concentration

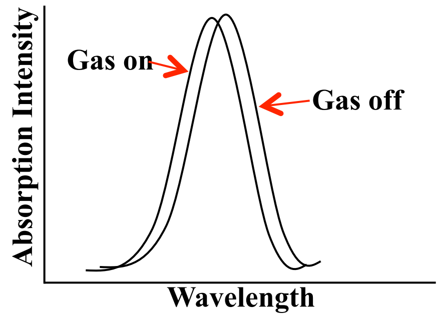


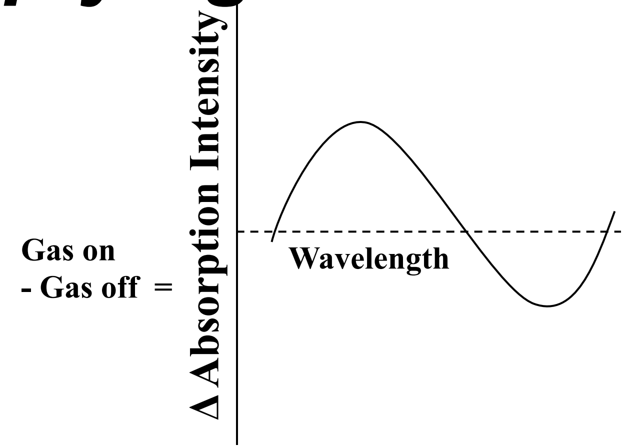
	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98

Challenging selectivity issues for CO and H_2!

Sensor Array Analysis: Applying PCA





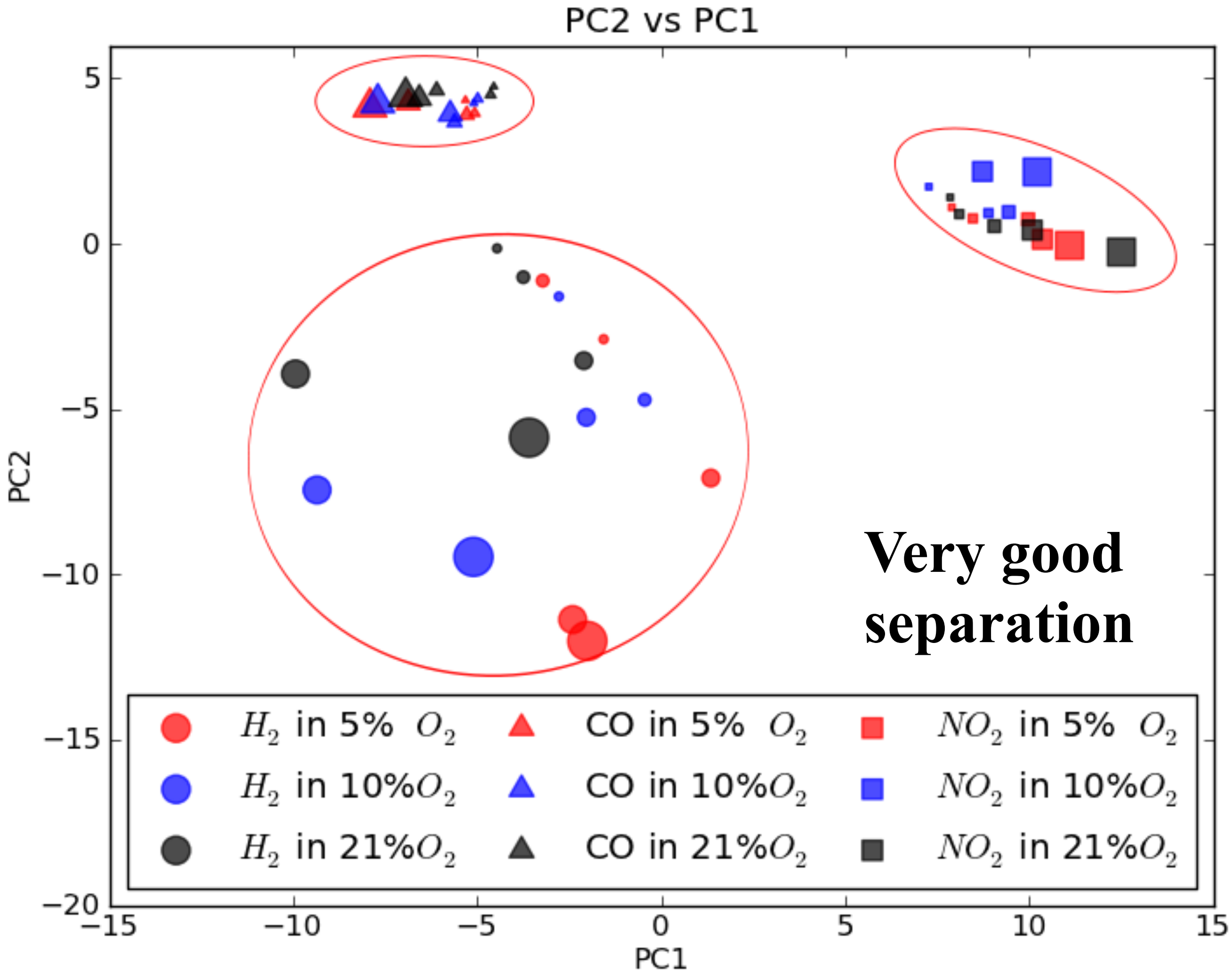


~390-1000nm = 630 *3 (sample #)

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

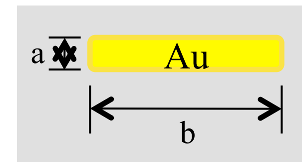


- 630 variables x 3 array elements = 1890 variables
- 45 observables (5 gas concentrations, 3 target gases & 3 [O_2]
- ~175 wavelengths used as inputs from the spectra

N. A. Joy, P. H. Rogers, M. I. Nandasiri, S. Thevuthasan, M. A. Carpenter, Analytical Chemistry, **84**, 10437, (2012)

Why Au Nanorods?

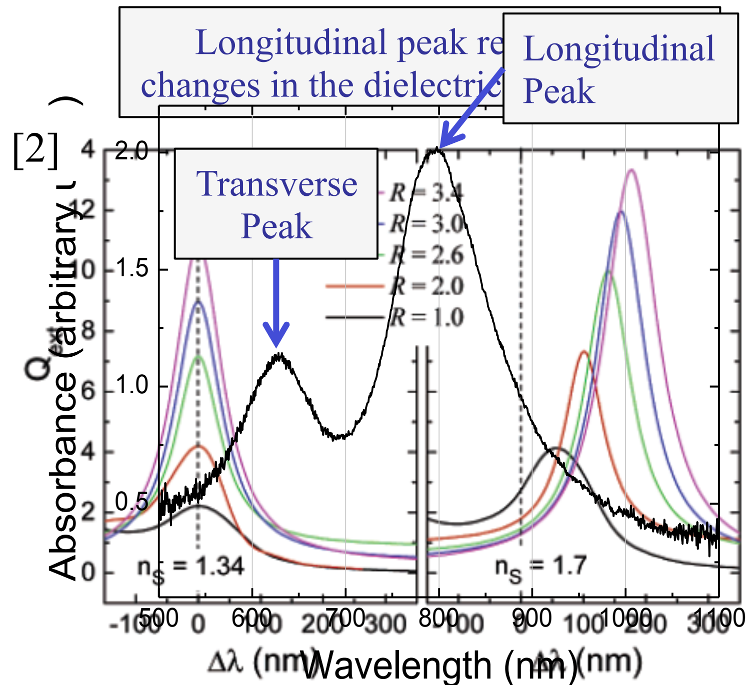
1. **Two SPR absorbance peaks**
2. **Tunable longitudinal peak position**
3. **Catalysis by gold nanoparticles is size dependent[1]**
4. **Sensitivity is shape dependent[2]**



aspect ratio = b/a

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.

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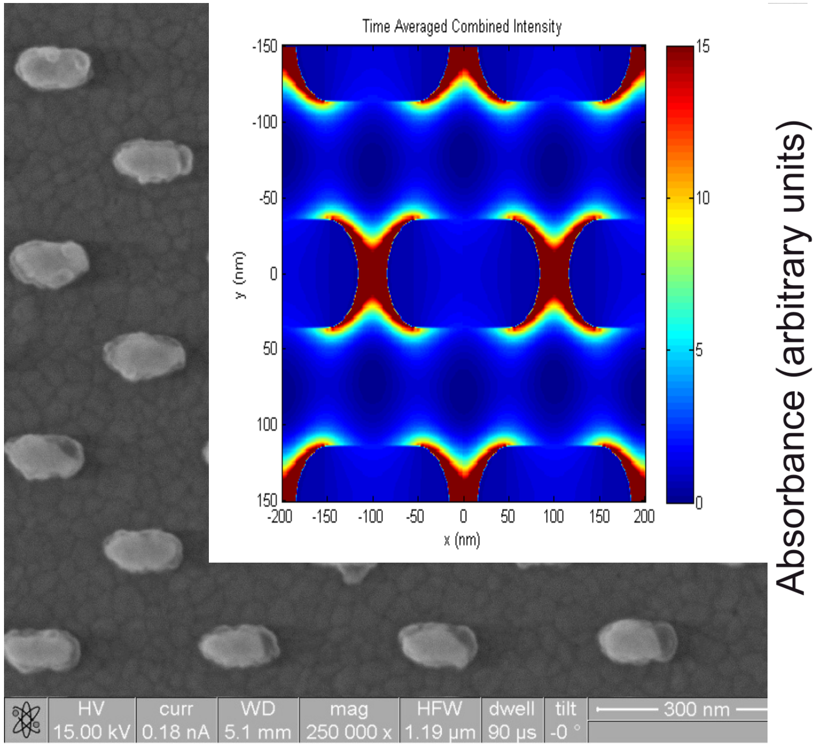
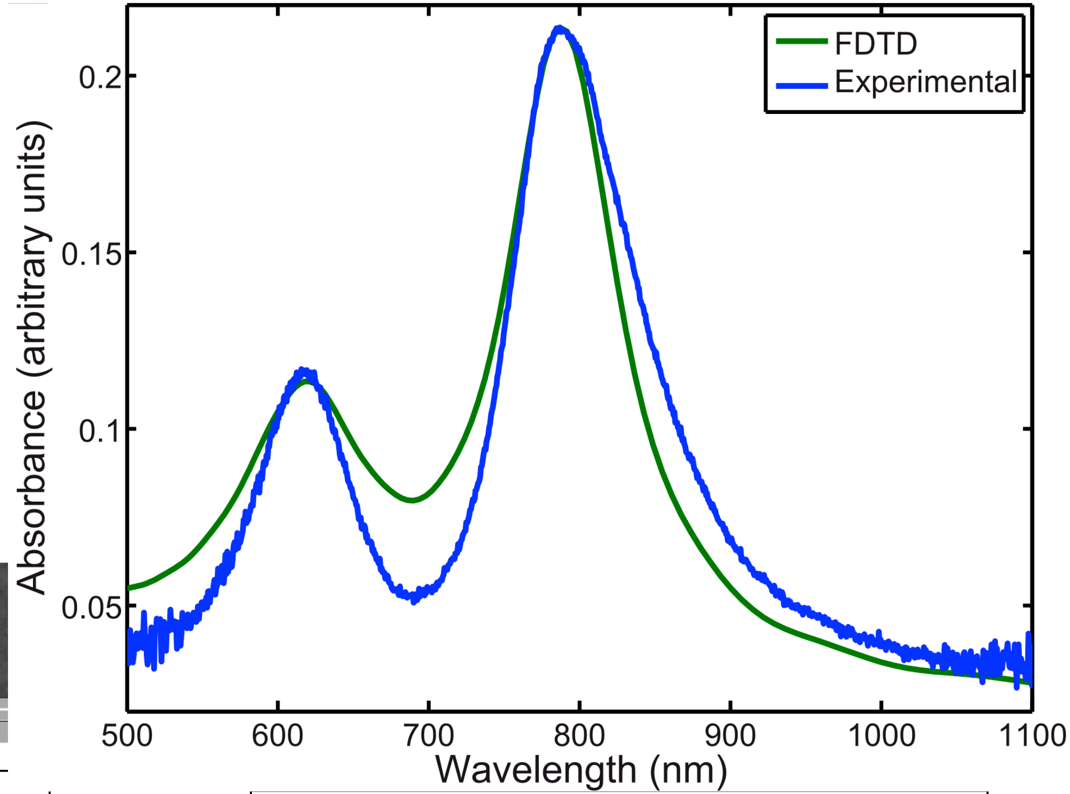
Summary of the Sample Used for Sensing Tests



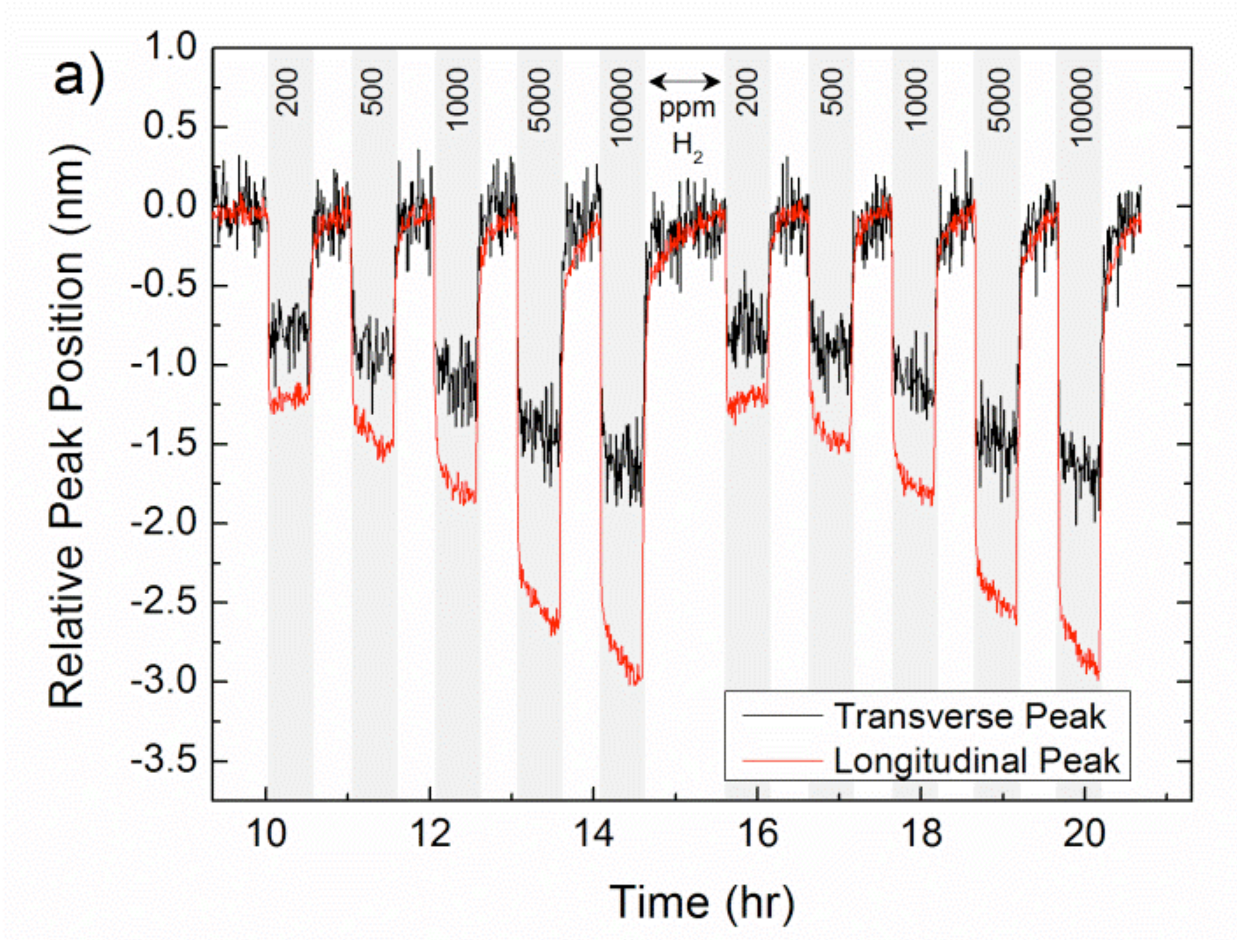


- 44 x 130 nm nominal dimensions
- 15 nm YSZ capping layer
- Annealed up to 600°C for 6 hours

- 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



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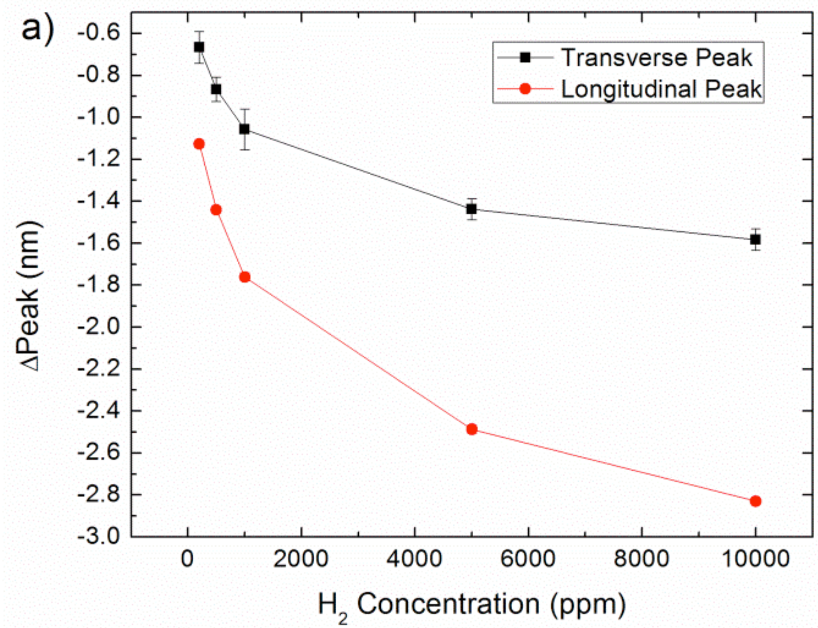
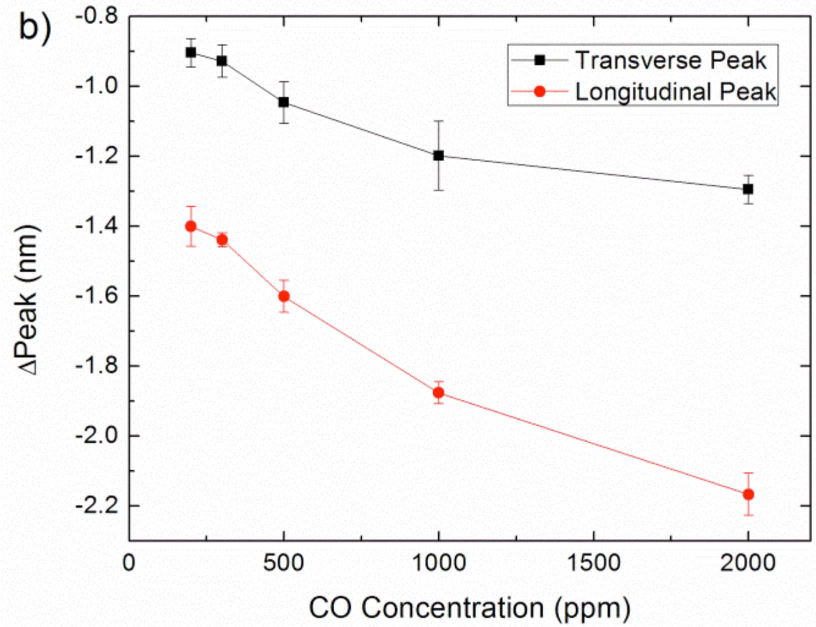
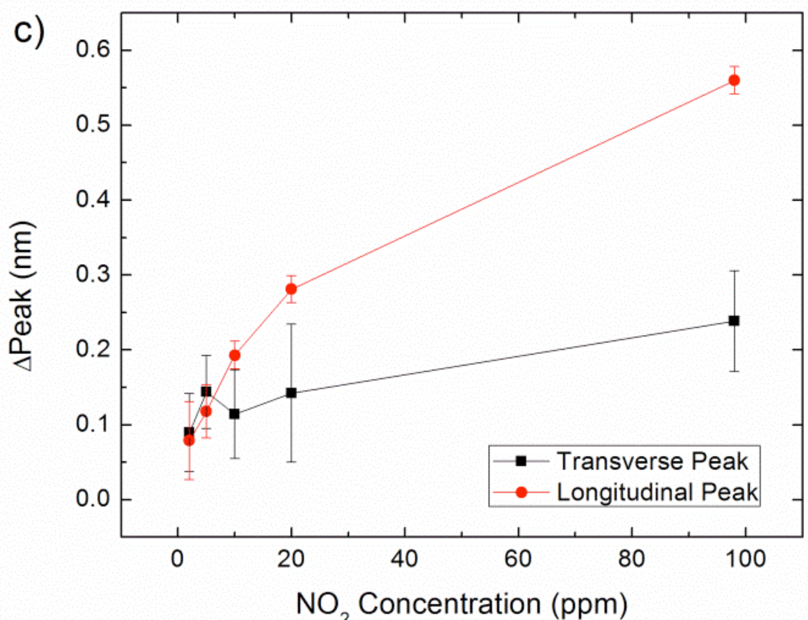
H_2, CO and NO_2 calibration curves for 44x130nm nanorod







Longitudinal mode is more sensitive in each case

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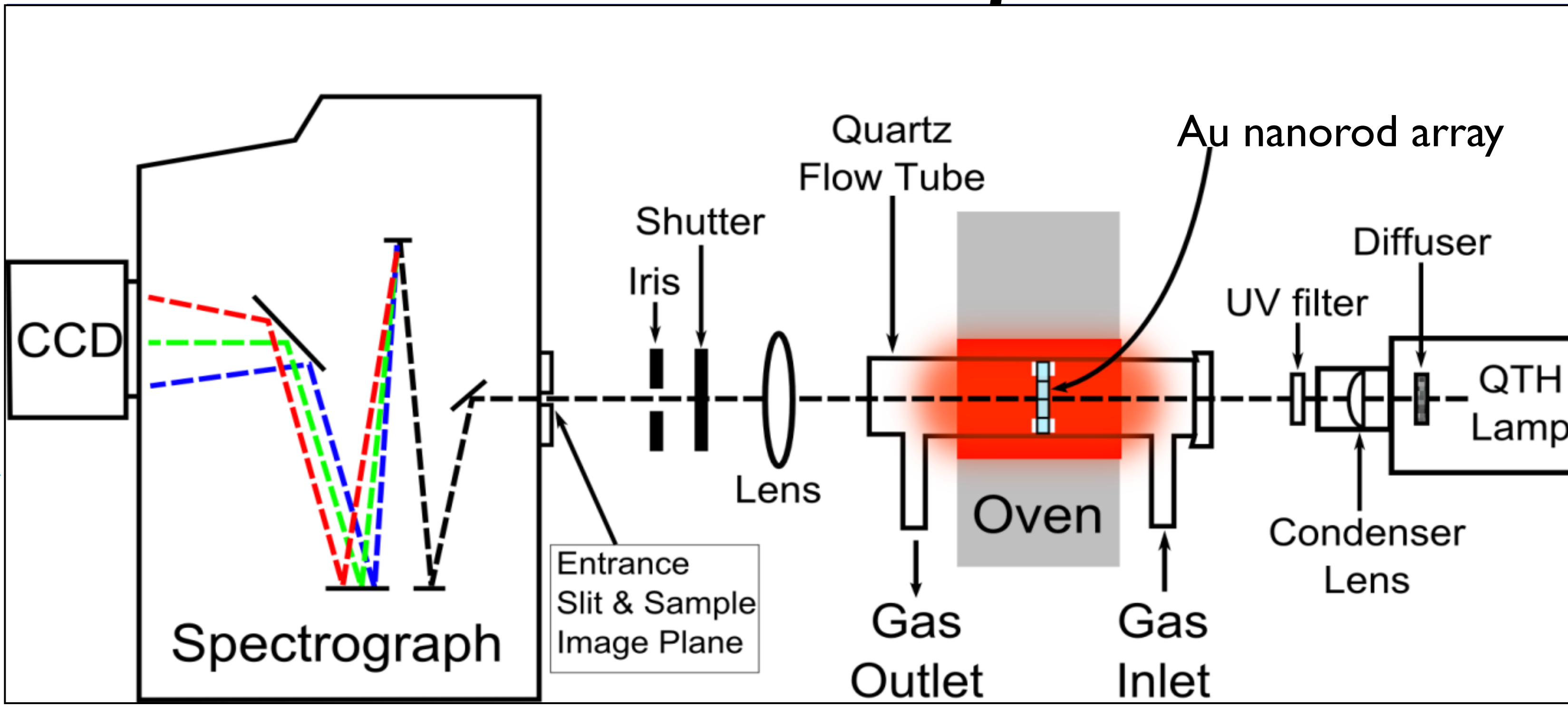
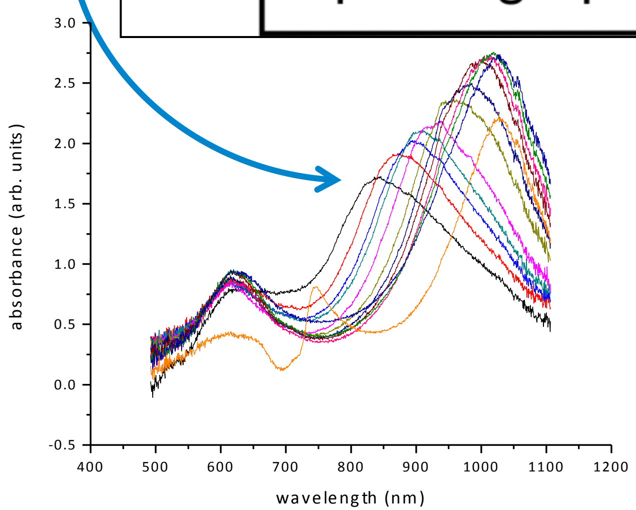
Setup for sensing experiments





- Gases tested : O_2, H_2, CO, NO_2
- Temperatures: ≤ 800^0C

Imaging nanorod arrays

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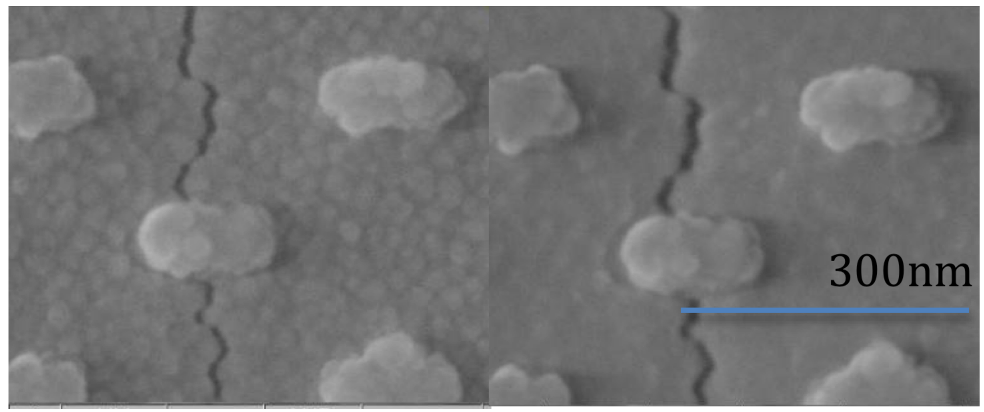
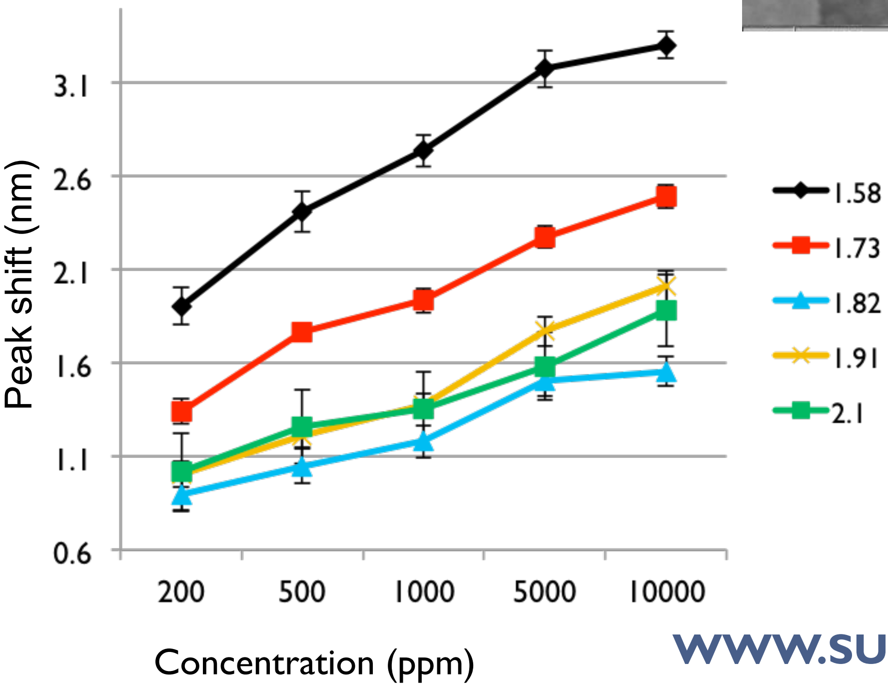
Sensing with improved geometry control

Before After



Sensing results to H_2:



- There is no trend that can be observed in the sensitivity with aspect ratio
- Need more control over the fine surface structure to enable clear trends as function of aspect ratio to be observed

Design and optimization of nanorods in parallel with bulls-eye work

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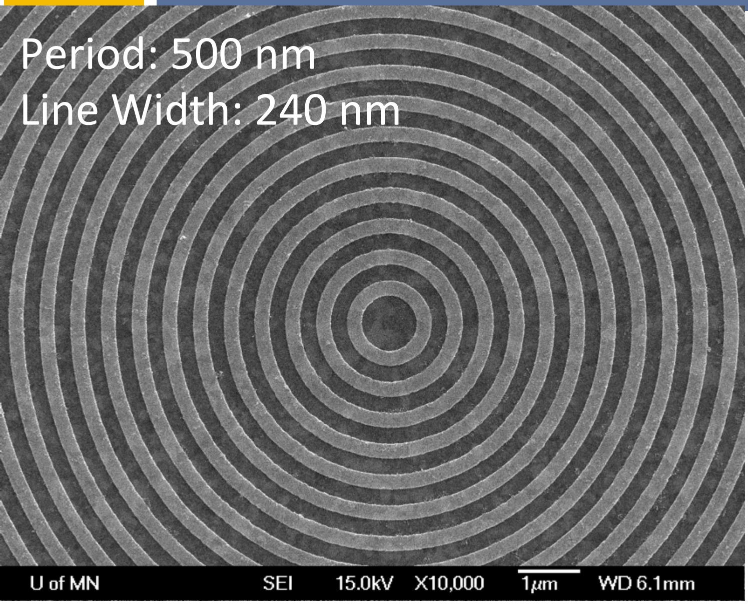
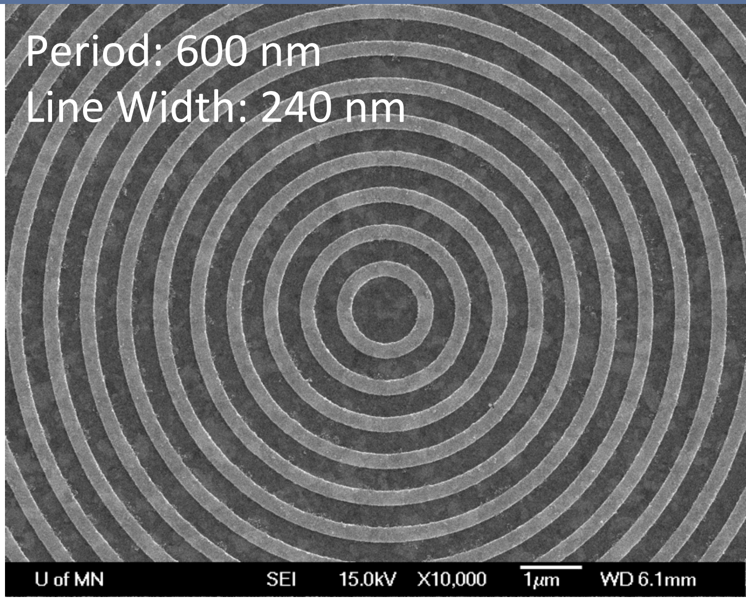
Varying the Bull's Eye Dimensions

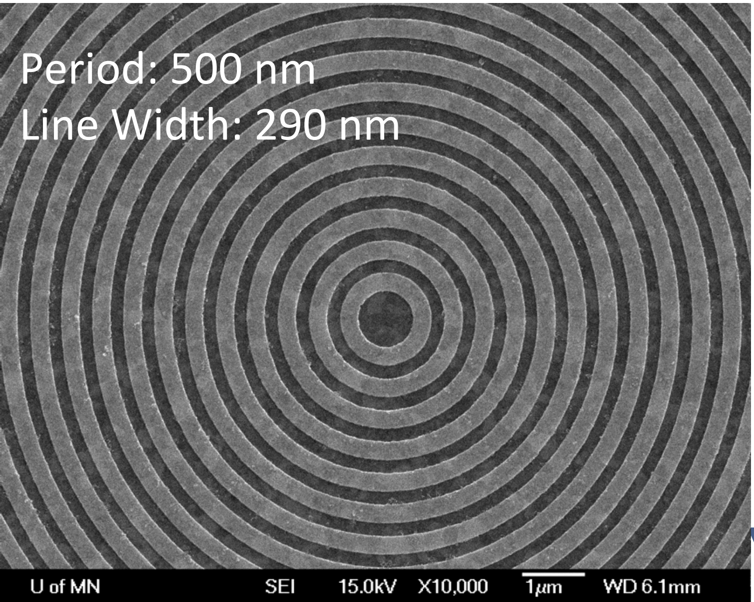


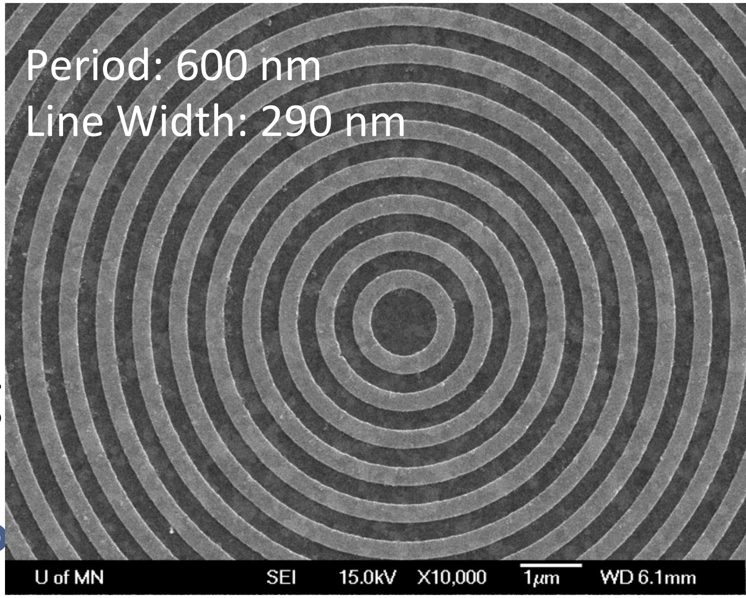


By changing the period and the line width of the grating the plasmonic spectra can be tuned to match that of the patterned nanorods

Thermal stability testing in progress

WW.SUNYCNSE.CO





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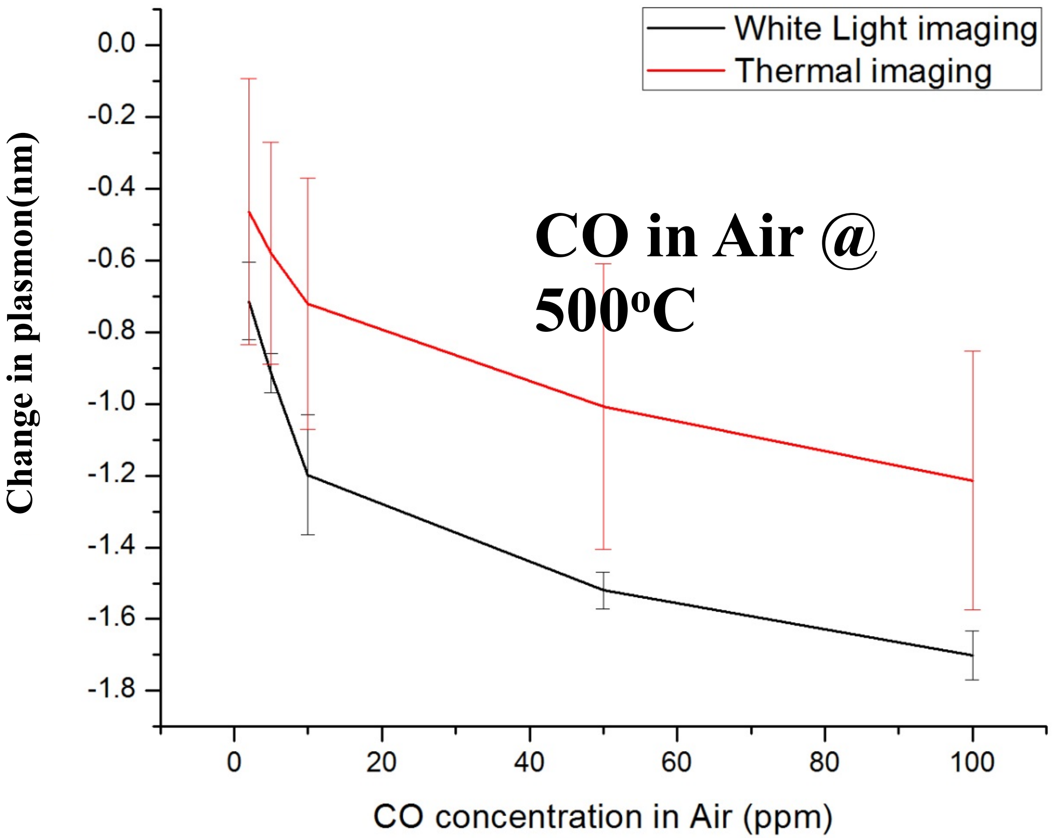
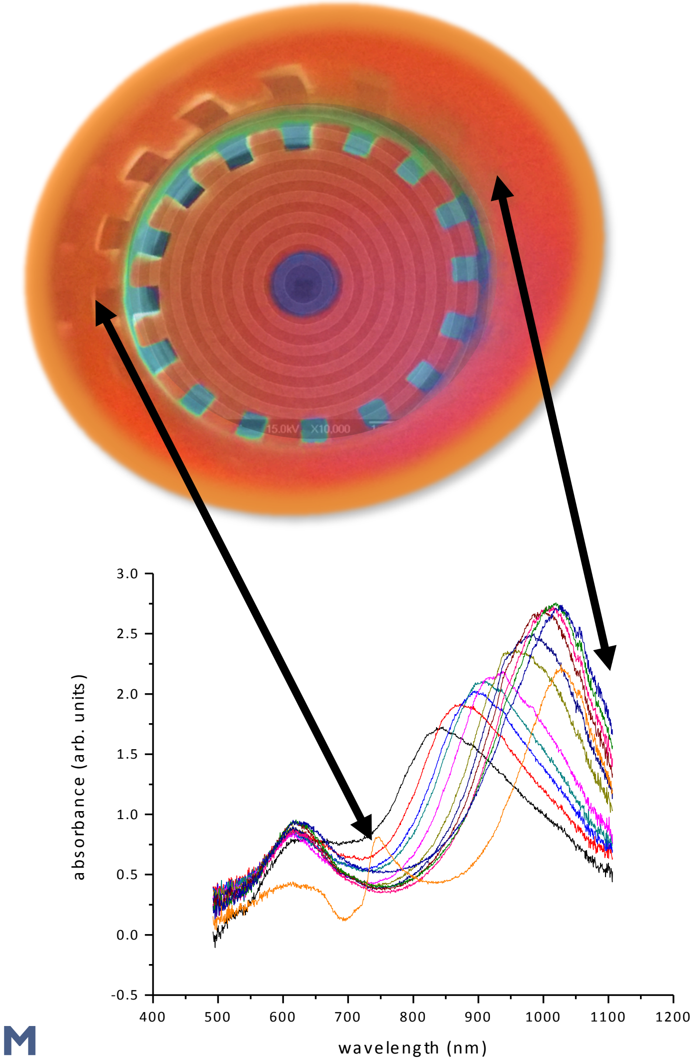
Energy Harvesting Sensing Data

Recent Results: Comparing Energy Harvested Sensing with Standard White Light Sensing Results





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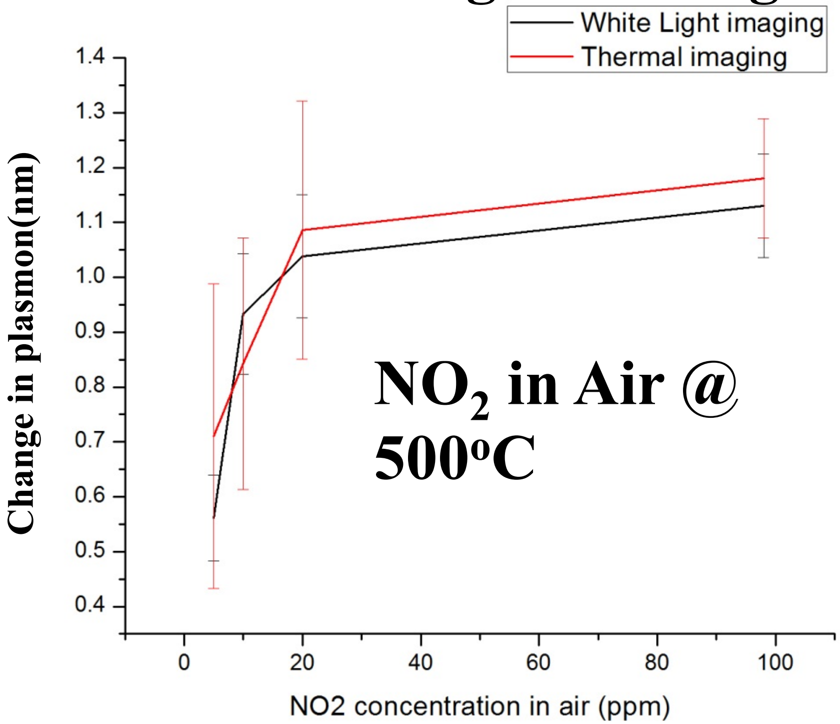

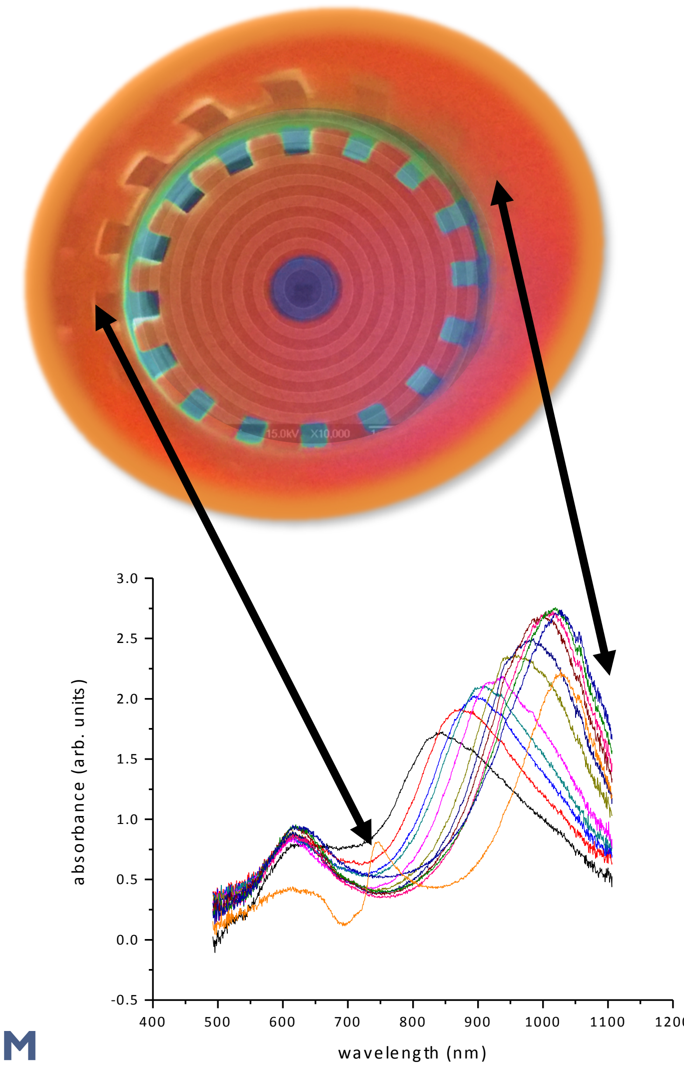

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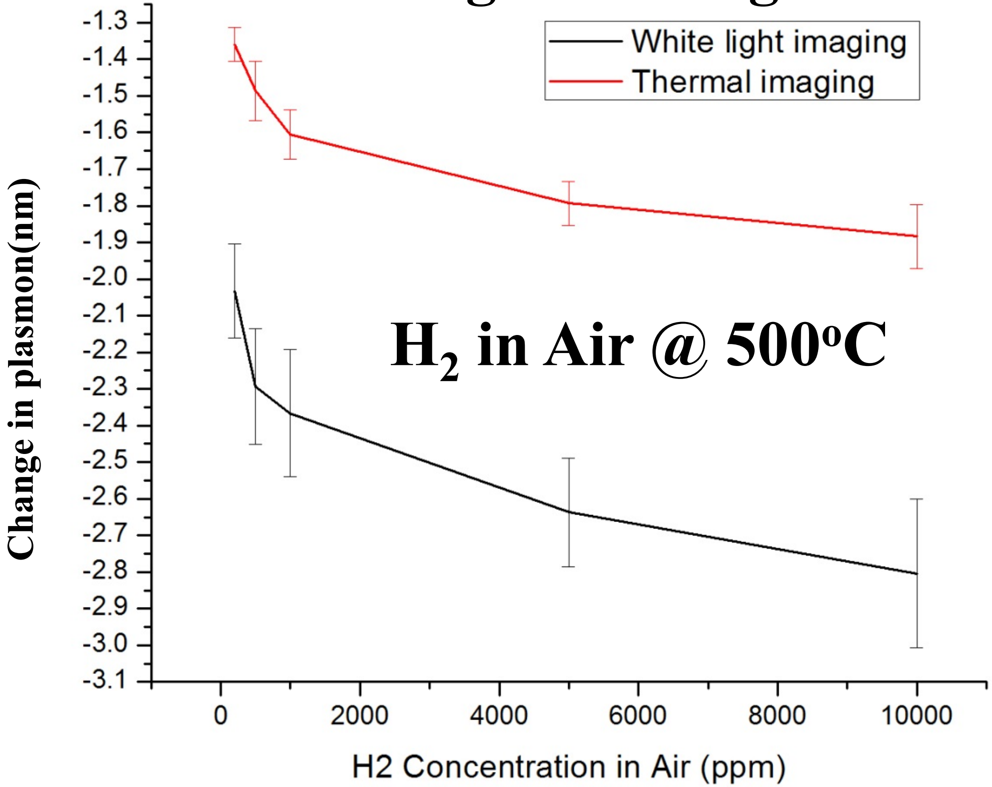
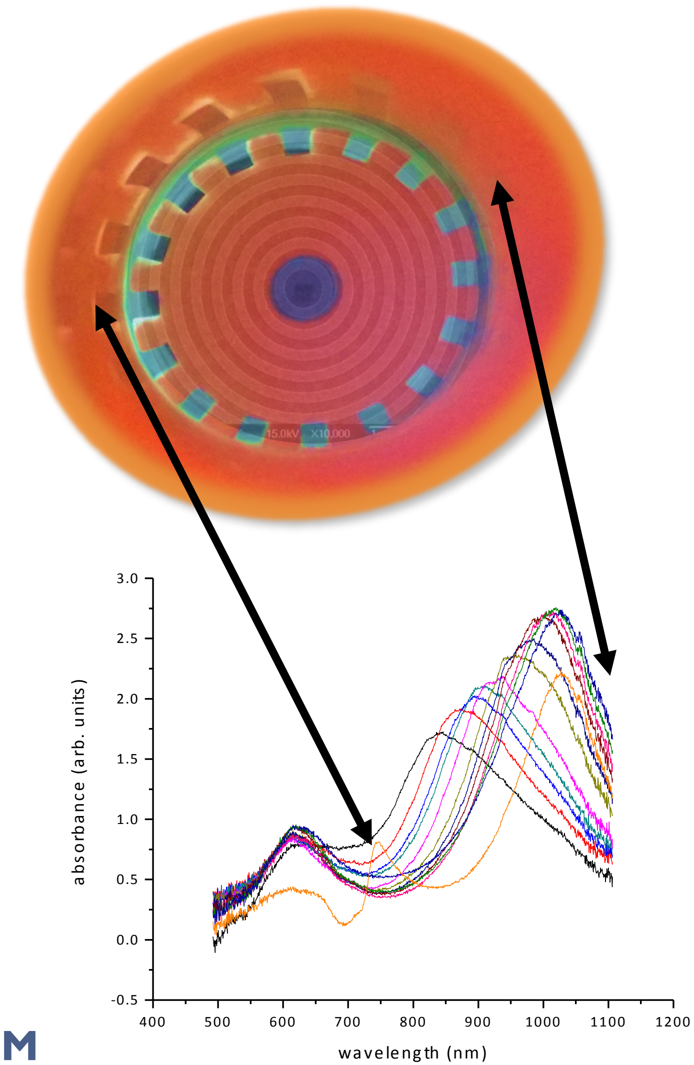
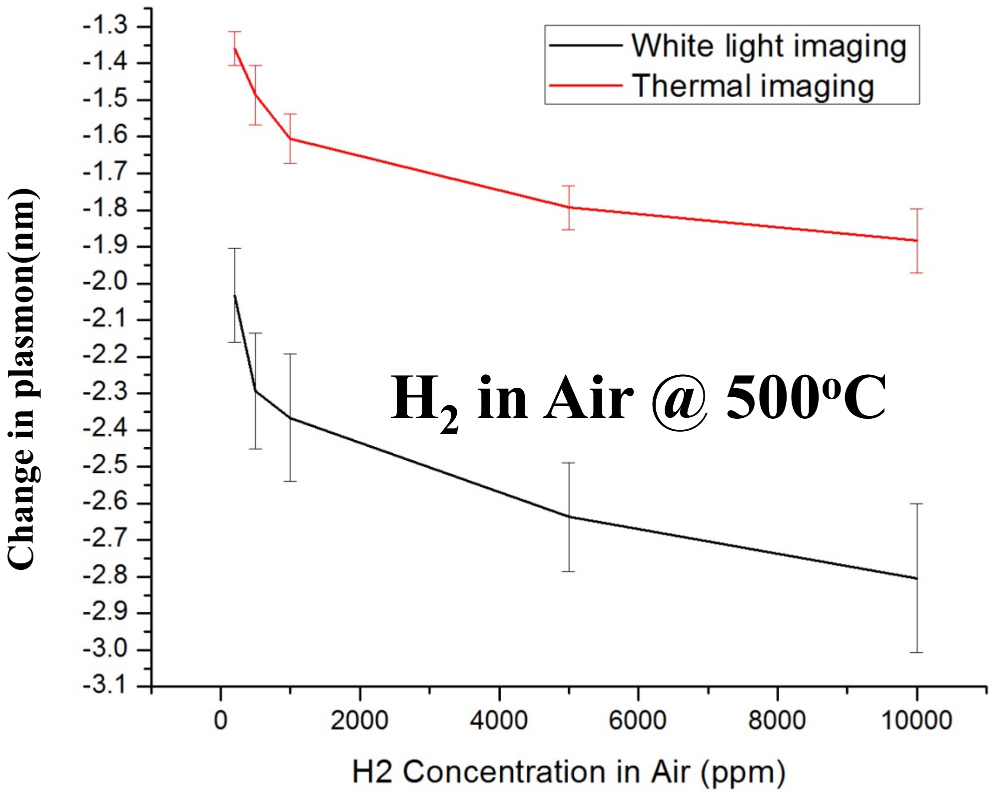
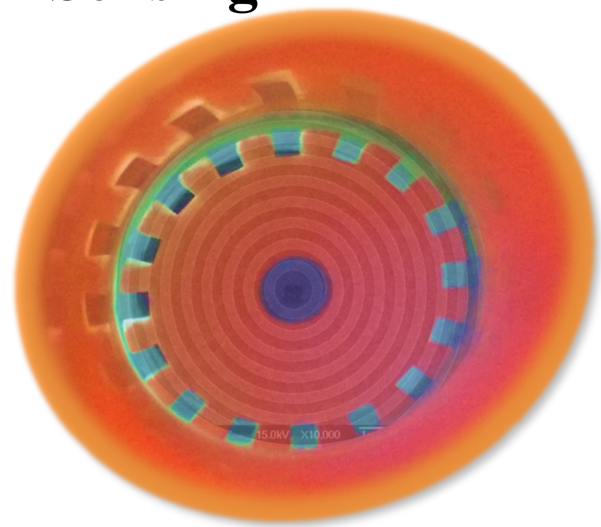




Energy Harvesting Sensing Data

Energy Harvested Plasmon-Based Chemical Sensing





- Selectivity will be demonstrated through use of arrays and statistical algorithms
- Reliability over 100hrs

- **Demonstrated for first time plasmon sensing results without the need for an outside light source – *thermal imaging enabled chemical sensing***
- **Integration of this approach into a fiber based packaged design is currently in progress in collaboration with UTAS**

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**
- **Demonstrated for first time plasmon sensing results without the need for an outside light source – thermal imaging enabled chemical sensing**
- **Integration of this approach into a packaged fiber based design is currently in progress in collaboration with UTAS**

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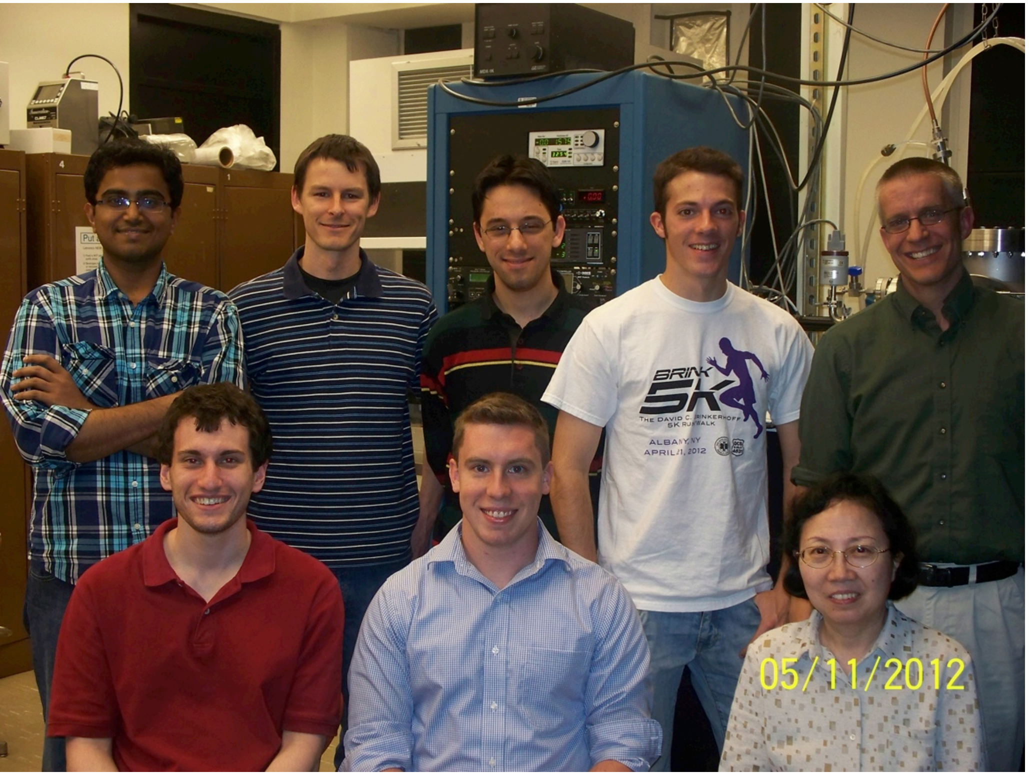
Acknowledgements



CNSE

Dr. Zhouying Zhao (Research Scientist)
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Dharmalingam, Gnanaprakash (Ph.D.)
Nick Karker (Ph.D.)
Vitor Rossi (Ph.D.)
Brian Janiszewski(UG)
Mike Briggs(UG)
Ryan O’Connor(UG)

University of Minnesota

Prof. Sang-Hyun Oh
Tim Johnson (Ph.D.) -graduated
Dan Klemme (Ph.D.)

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