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Thermal Energy Harvesting Plasmonics Based Chemical Sensors

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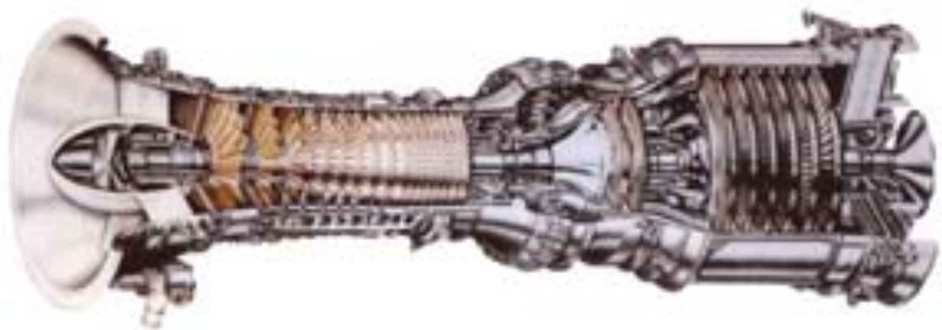
Harsh Environment Chemical Sensors

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

Nanocomposite Materials

•Optical analysis of Au and Ag SPR bands
•YSZ matrix material
•500-800°C operating environment
•SOFC, Jet engines, turbines
•CO, H_2, O_2, NO_x, R_xS



Goals of Research are Three-Fold

1. Develop prototype materials for use in next generation sensing devices
   - Sensitivity, reliability, selectivity
2. Determine fundamental material properties/dynamics/kinetics which govern the sensing mechanism
3. Develop new sensing strategies and paradigms

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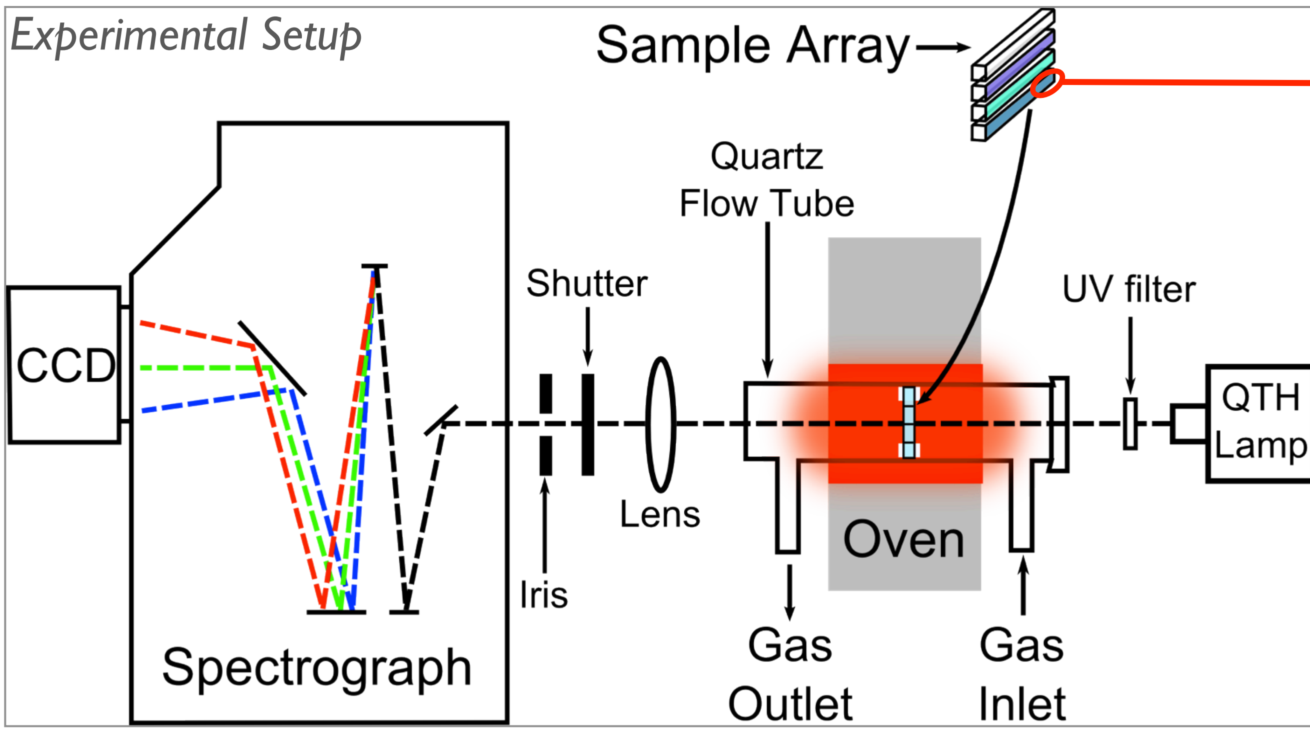
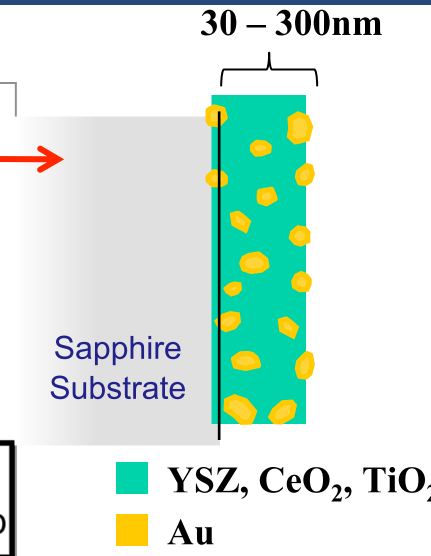
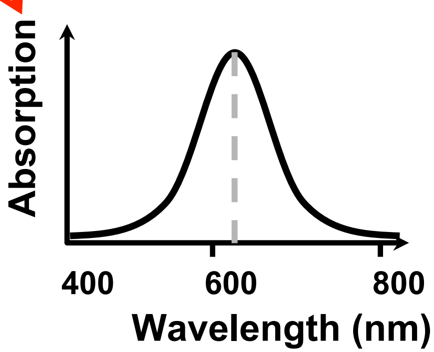
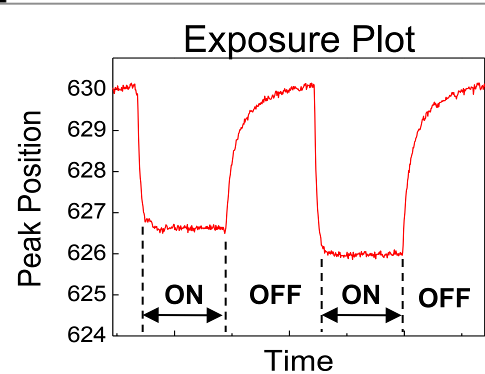
General Overview of Plasmonics Lab Bench



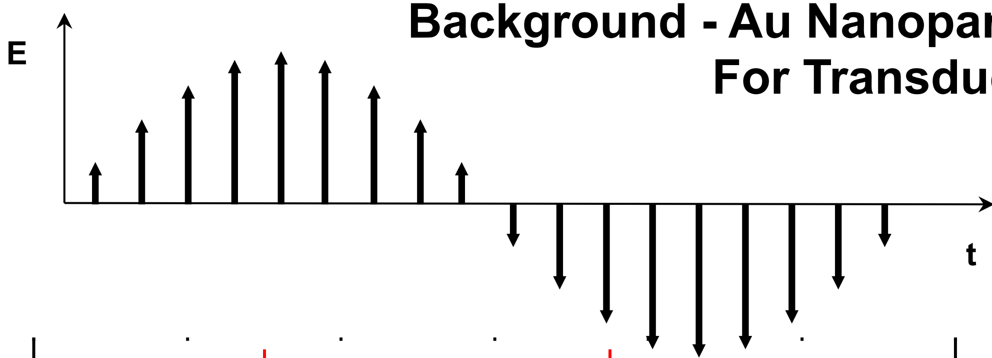


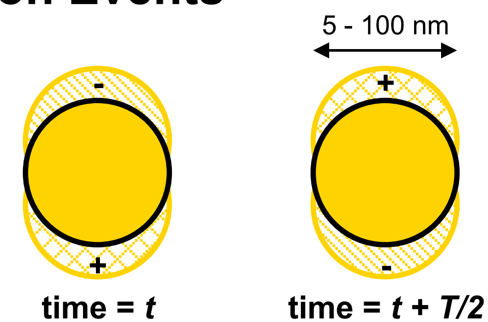


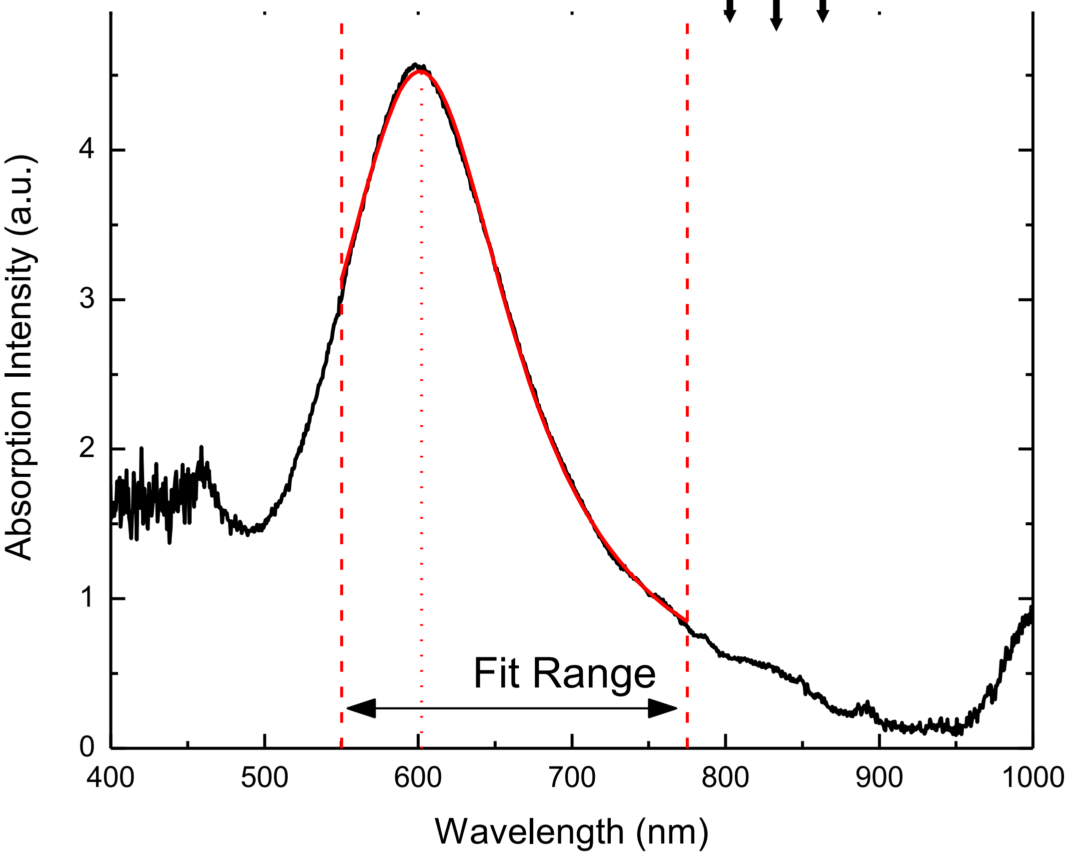


YSZ = Yttria Stabilized Zirconia

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

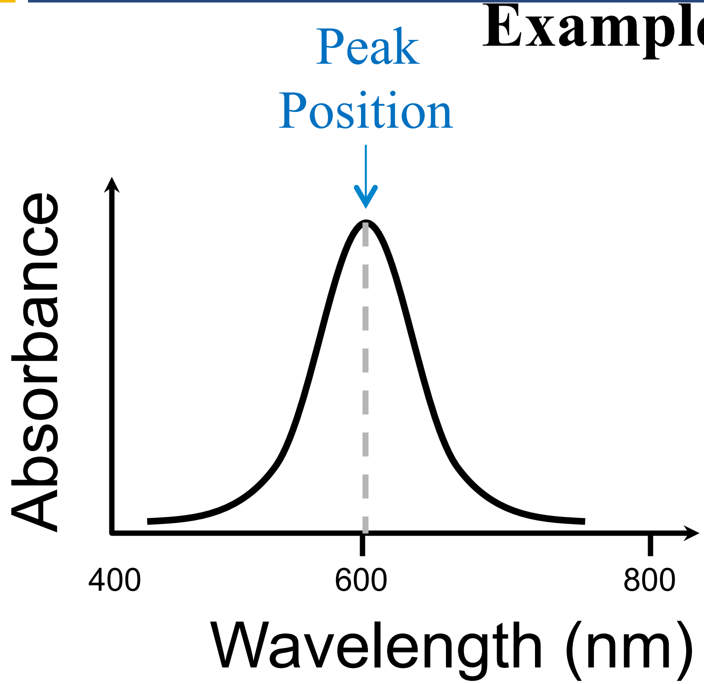
ε_m - matrix (YSZ) dielectric constant

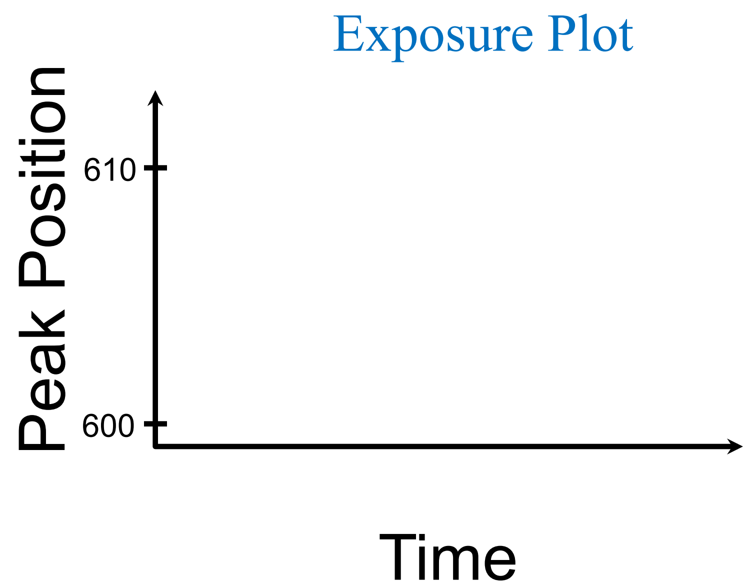
$\chi^{ib}(\Omega)$ - Interband trans. dielectric const.

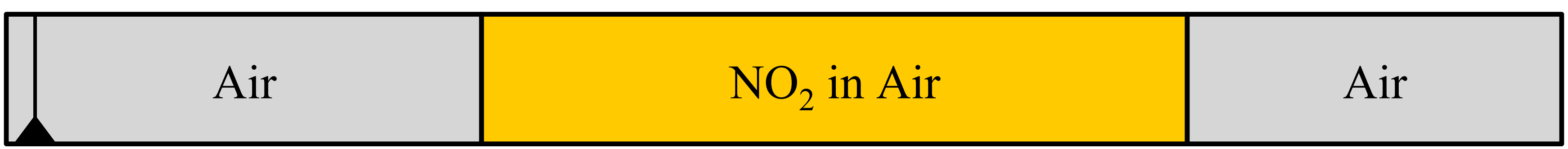
R - particle radius

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 } Reducing
CO } Reducing
NO_2 — Oxidizing

Rogers, P. H.; Sirinakis, G.; Carpenter, M. A. J. Phys. Chem. C **2008**, *112*, 6749
Rogers, P. H., Sirinakis, G., Carpenter, M. A., J.Phys. Chem. C, **112**, 8784-90 (2008).
Baltrus, J. P.; Ohodnicki, P. R.; Joy, N. A.; Carpenter, M. A.; Appl. Surf. Sci., 313, 19-25 (2014).

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

G. Dharmalingam, N. A. Joy, B. Grisafe, M. A. Carpenter, Beilstein Journal of Nanotechnology, **3**, 712 (2012)

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Sensor Array Studies: Material Control

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

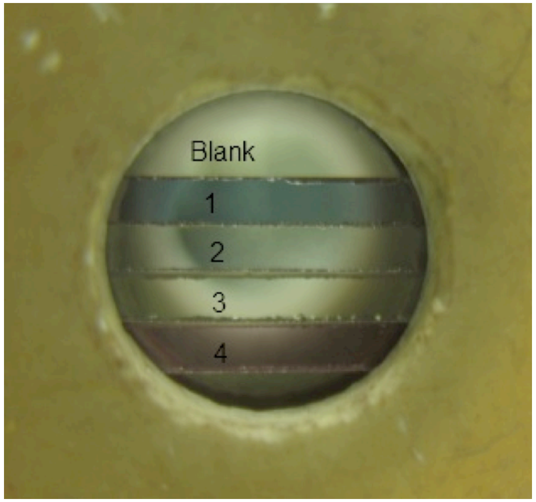
- Ceria is 200nm thick
- Gold is implanted to depth of ~75nm
- Post annealed to 1000°C
- Gold particle size ~30nm
- Au ~ 8 at. %

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

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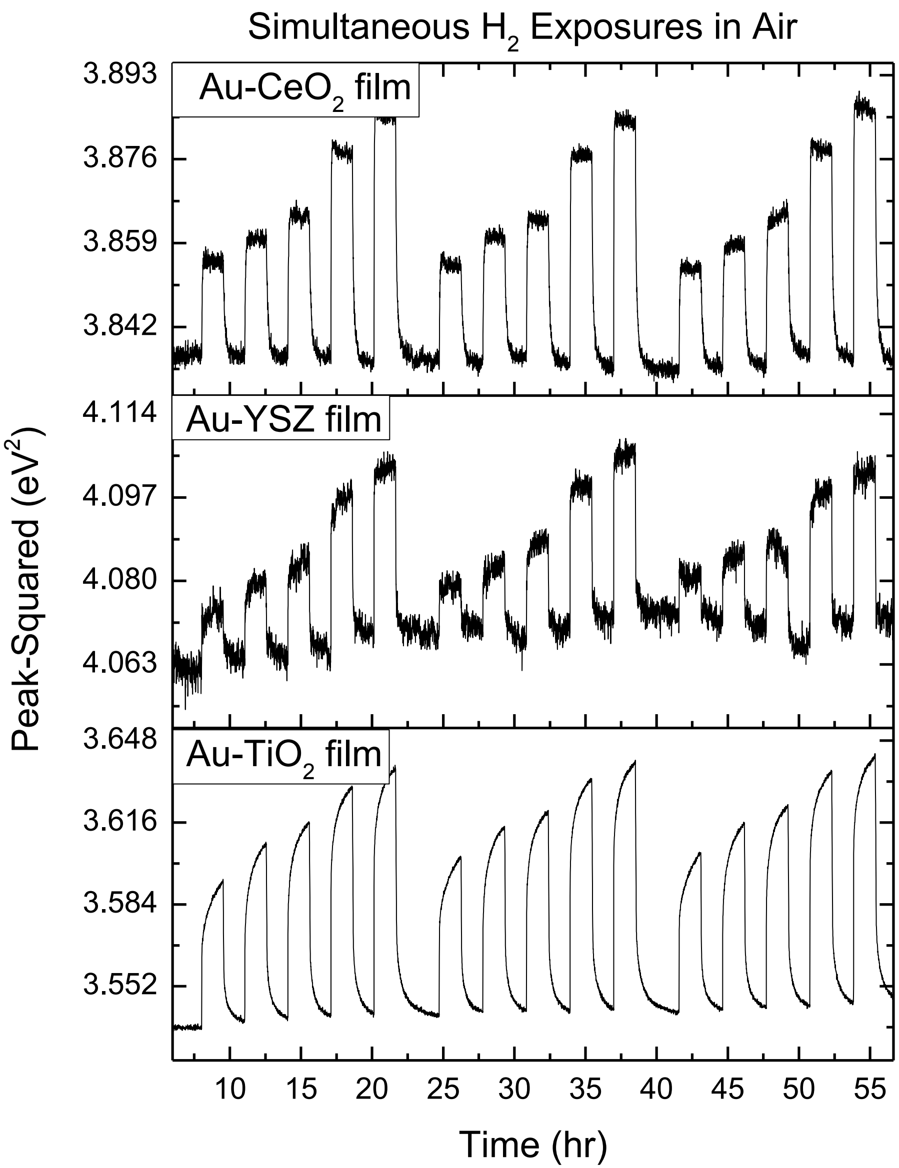
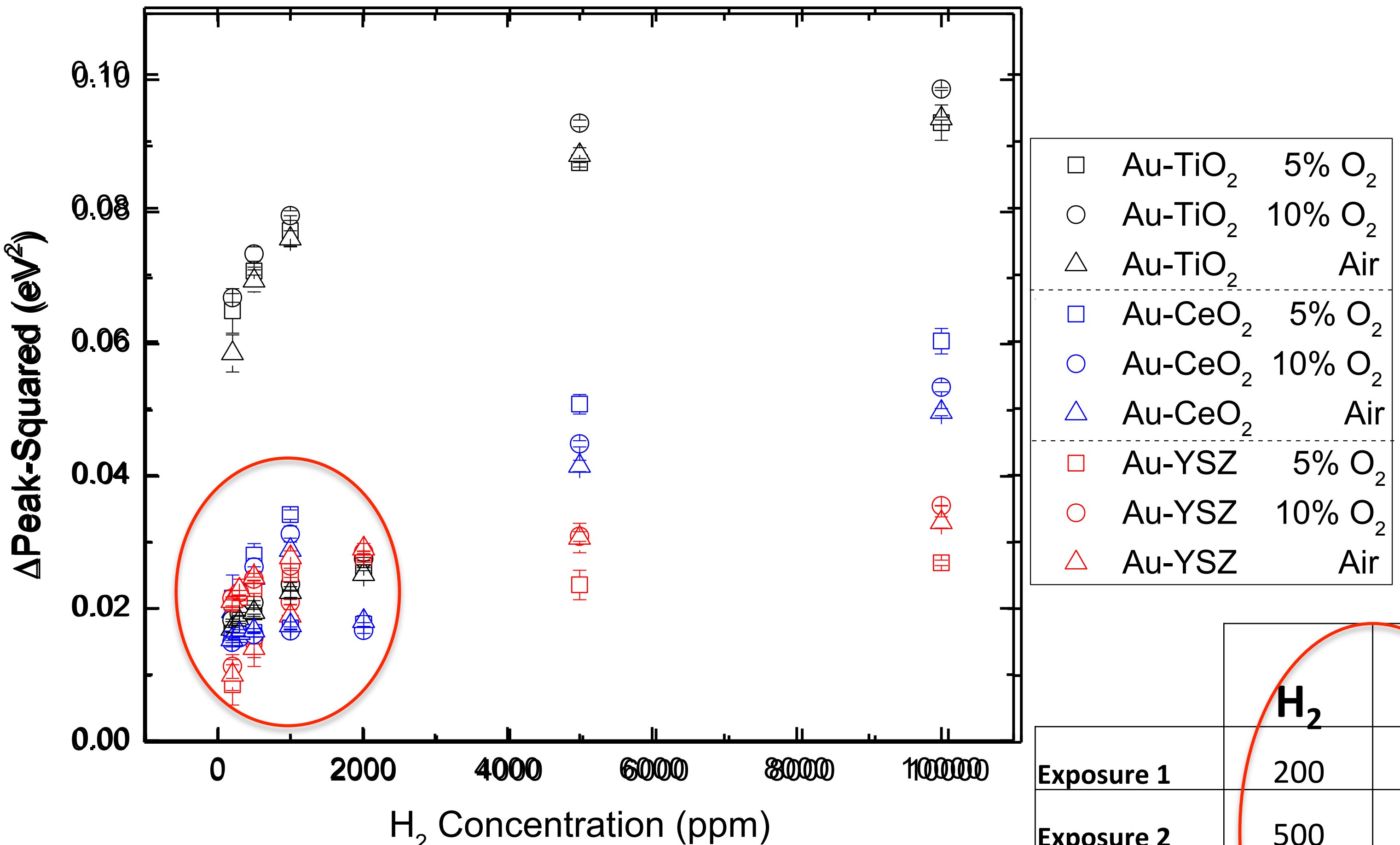
	H_2	CO	NO_2
Exposure 1	200	200	2
Exposure 2	500	300	5
Exposure 3	1000	500	10
Exposure 4	5000	1000	20
Exposure 5	10000	2000	98



H_2 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!

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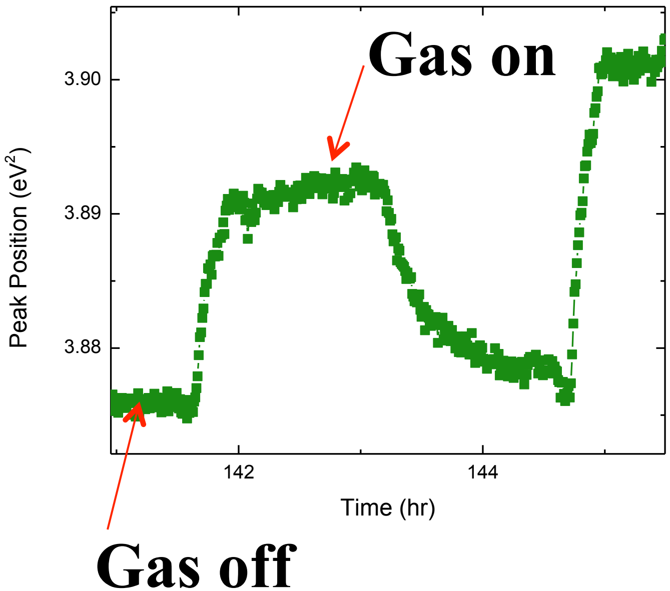
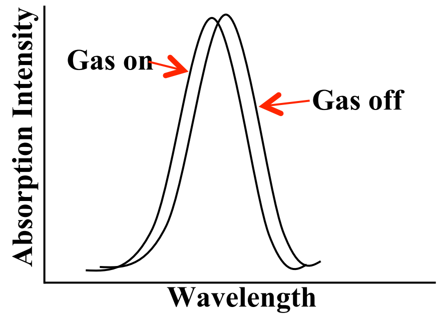
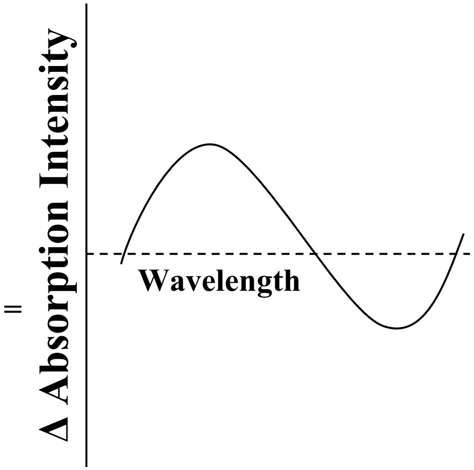
Sensor Array Analysis: Applying PCA





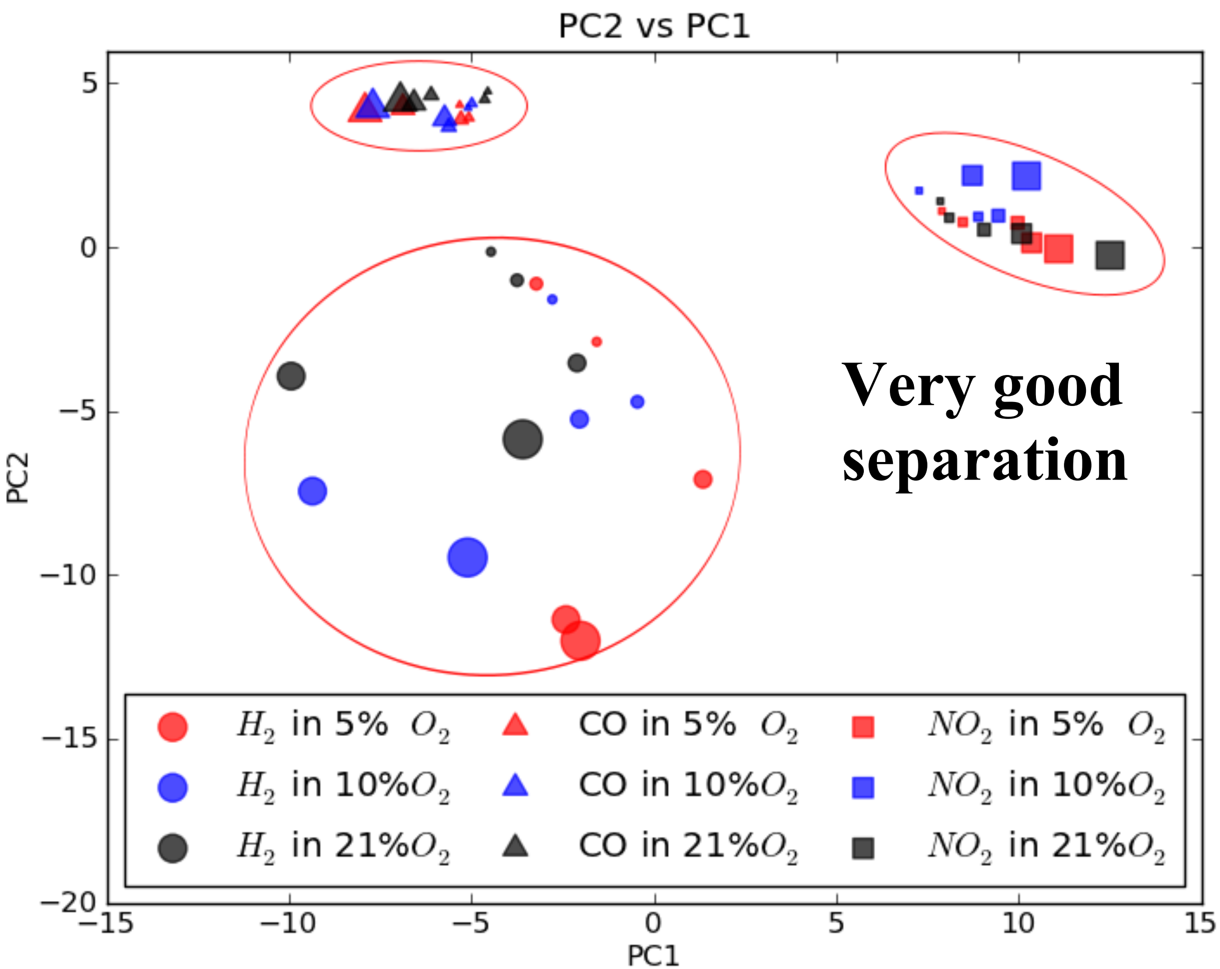


~390-1000nm = 630 variables

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
		500	0.46479	-0.19218	-0.28943	-0.27595	0.145434	-0.13233	0.203813	0.0

45 Observations:
5 concentrations
3 Analytes
3 O_2 backgrounds

PCA Analysis of Sensor Array Data

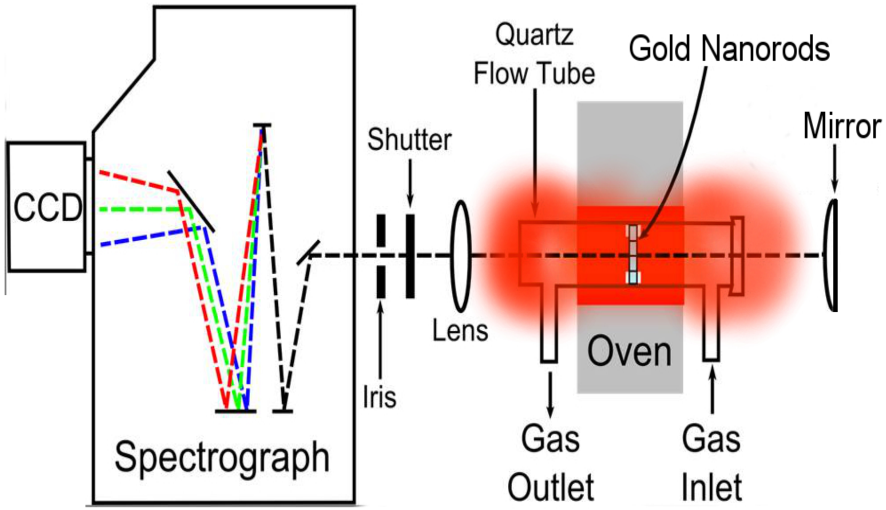


- **630 variables x 3 array elements = 1890 variables**
- **45 observations (5 gas concentrations, 3 target gases & 3 [O_2])**
- **Greater separation in PCA space**

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

Integration challenges for Plasmonics based sensors

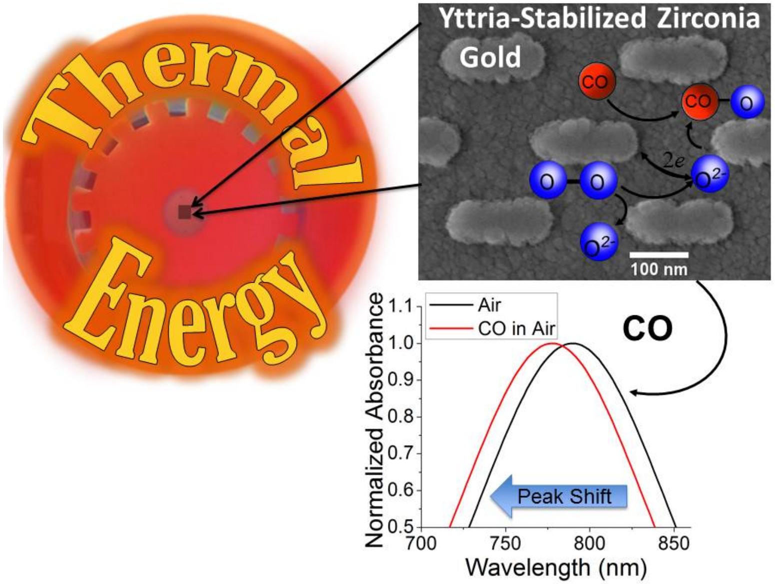
Thermal energy harvesting plasmonic based chemical sensors



General Methodology

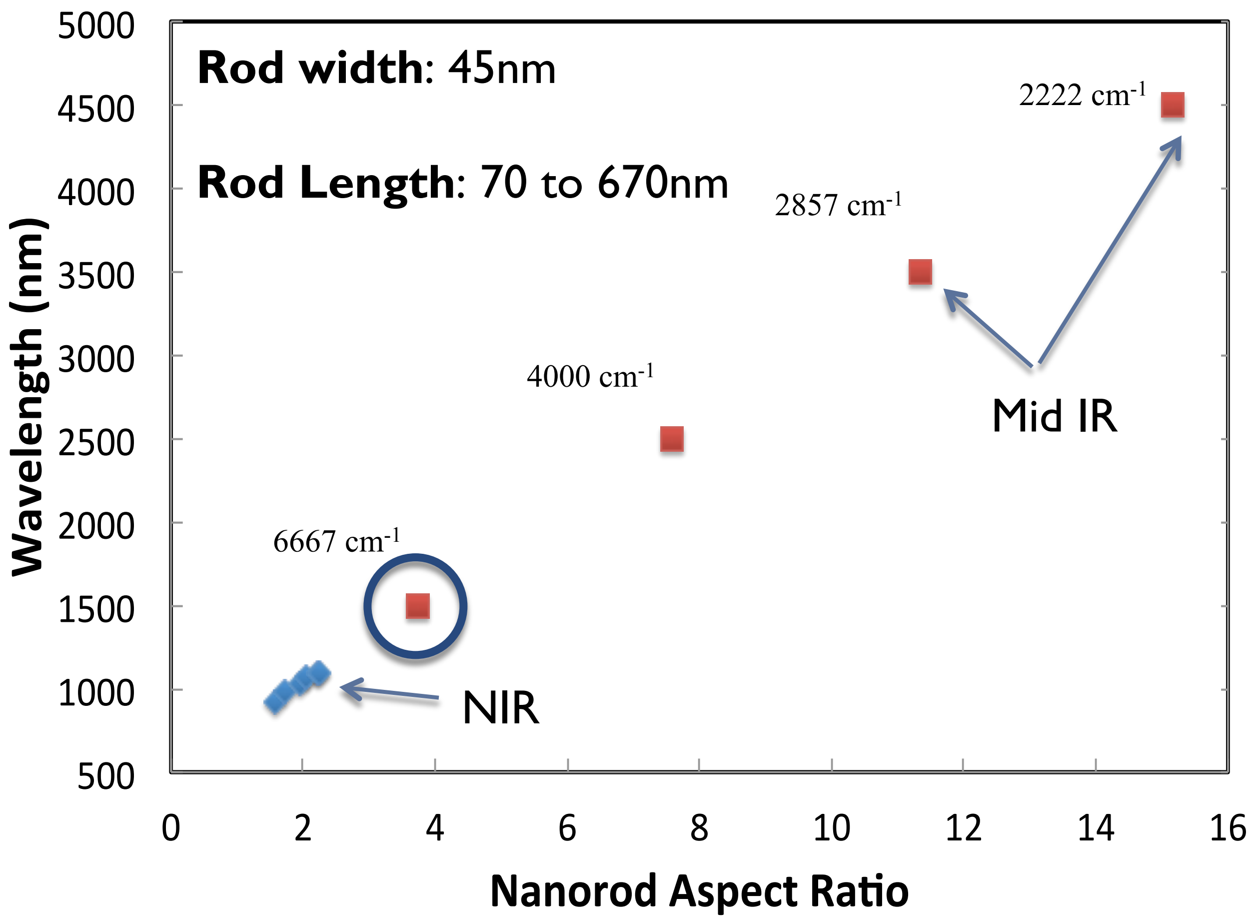
- *No external incident light source needed*
- *Only requires thermal energy and an emission gas sensitive sample that absorbs the thermal energy*

- Sample placed in tube furnace which is at 600C
- Sample position is in location where temperature is 500C
- CCD spectrometer images both bare quartz substrate for reference of thermal energy as well as nanorod sample
- Measures absorbance spectra as function of time and gas exposure



N. Karker, G. Dharmalingam, M. A. Carpenter, ACS Nano, **8**, 10953 (2014).

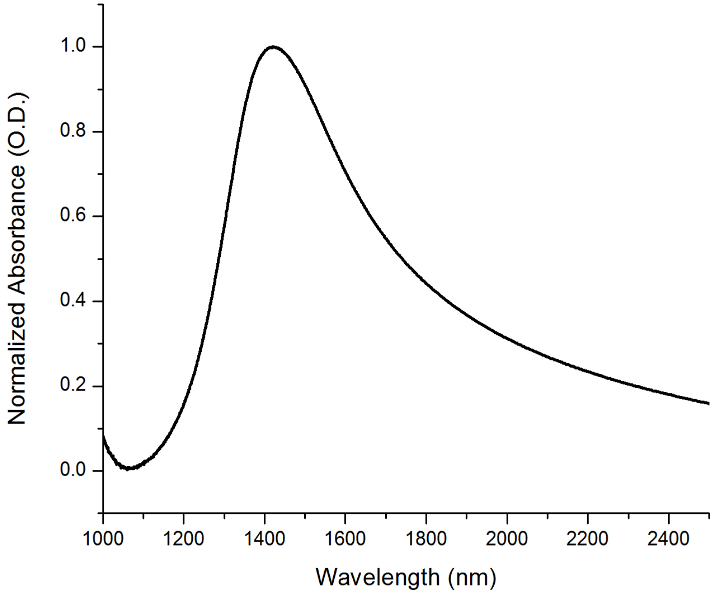
Tuning the NR to Thermal Energy

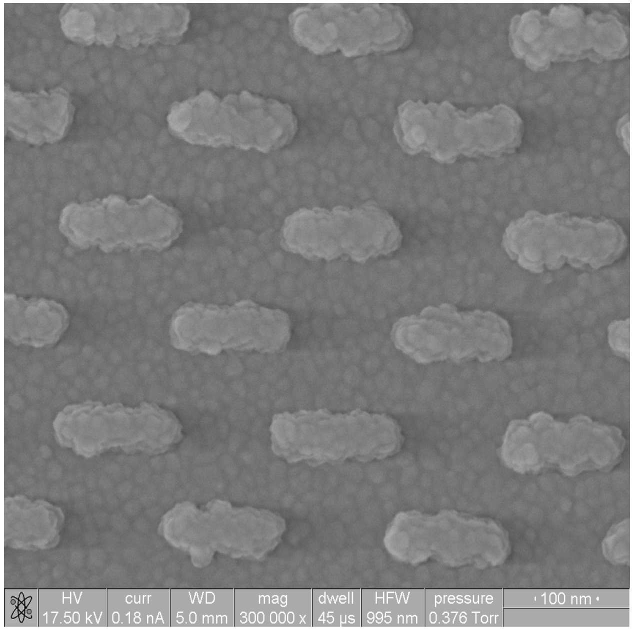


Aspect ratio = Length / width

- Higher aspect ratio rods absorb further into NIR-mid IR
- Potential for lowering energy harvesting operation temperature
- Tune interfacial chemistry to enable energy harvesting chemical sensor at a range of temperatures

Thermal Energy Harvesting – NIR

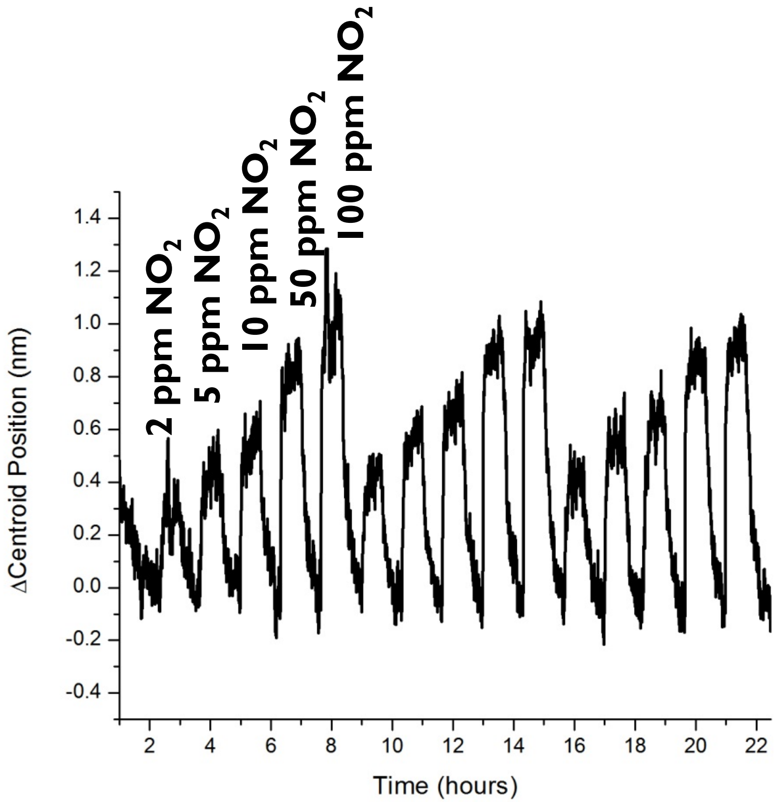




- Room temperature NIR spectra showing the longitudinal plasmon peak of the ebeam lithography patterned 44x170nm Au nanorod sample.
- eSEM image of the 44x170nm Au nanorod sample.

Sensing Data: Air-NO_2 Experiment

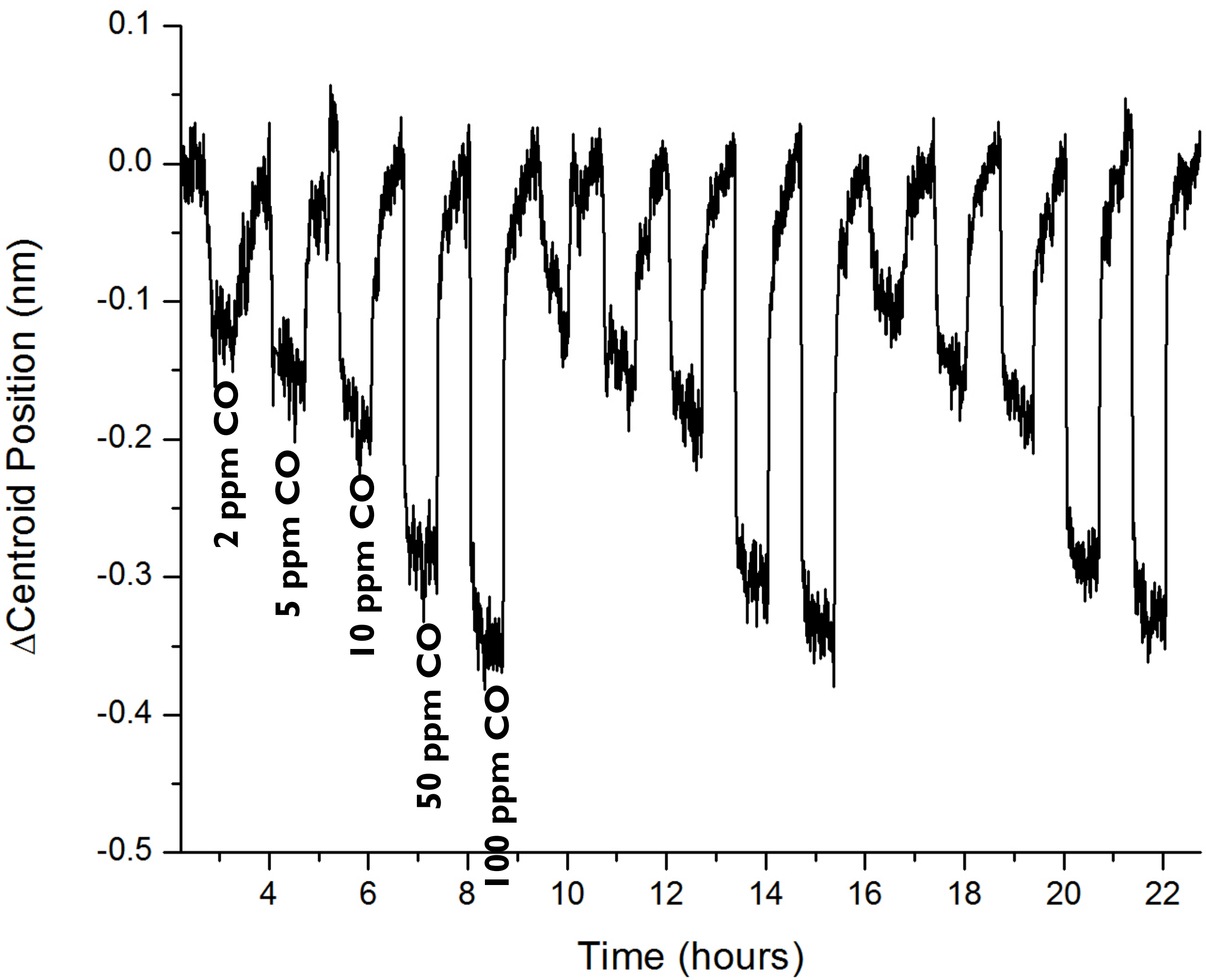
Uses Real-time I_o, Baseline corrected



500C

Sensing Data: Air-CO Experiment

Uses Real-time I_o, Baseline corrected



500C

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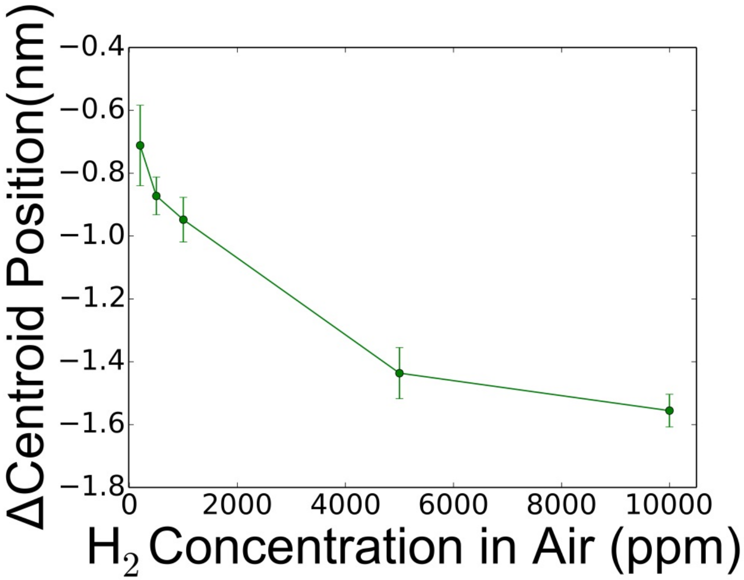
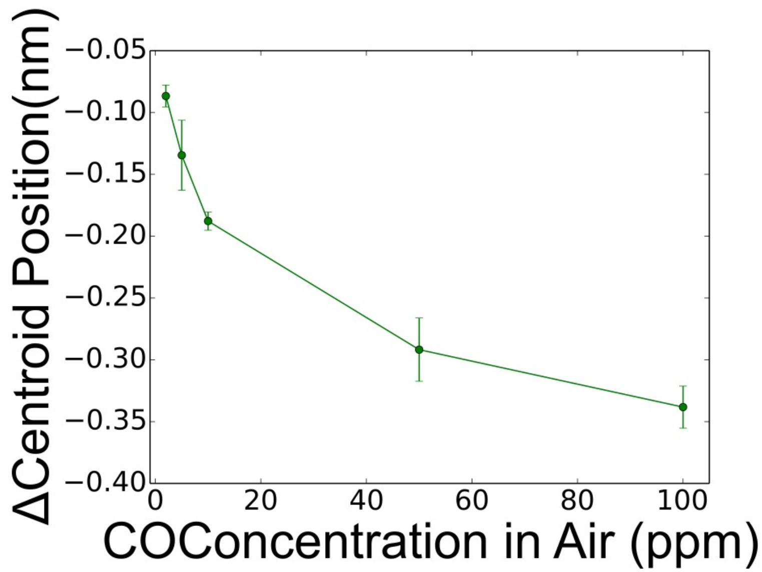
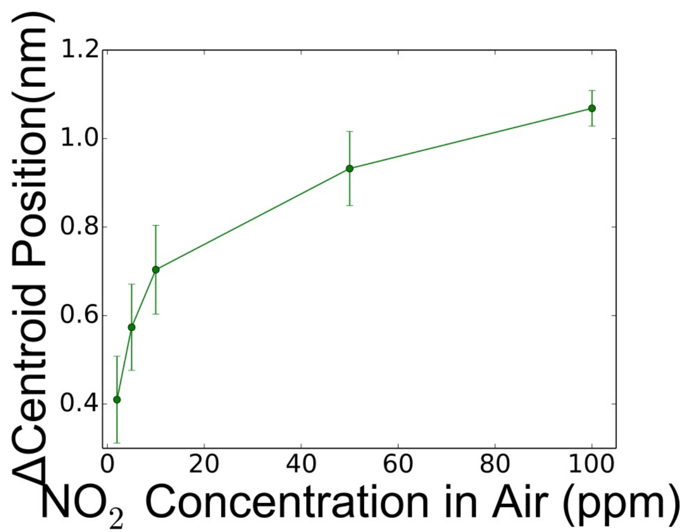
Calibration curves

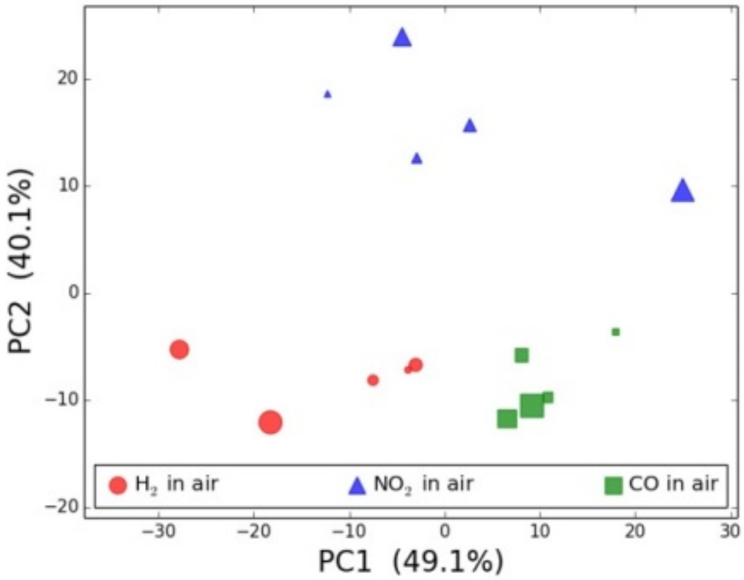




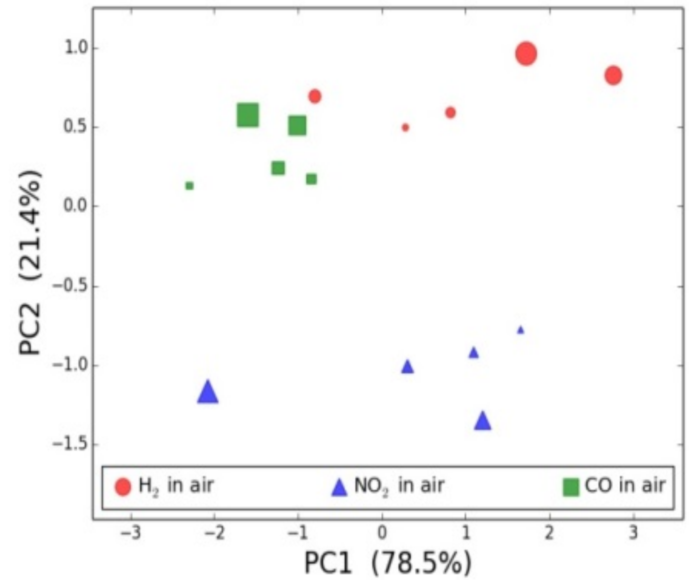
Averages 15 values



PCA analysis- Selectivity



(a) **Full spectrum PCA** performed on wavelength range of 1150nm-1600nm.



(b) **Reduced wavelength PCA** uses wavelengths of 1325, 1410, 1450nm **with similar selectivity** as with the full spectrum PCA.

- Integration is further simplified if through the use of a select number of wavelengths, the target gases of interest can be detected with the requisite selectivity
- In summary, these results prove that there is no need for either a white light source or a spectrometer to selectively detect emission gases under harsh environment conditions

Action Items: *1) Design of integrated assembly, 2) Optimization of NIR thermal energy harvesting methods, 3) Optimize selectivity in gas mixtures*

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
- Demonstrated for the first time the plasmonics based thermal energy harvesting enabled chemical sensors
- Integration of this approach into a packaged fiber based design is currently in progress in collaboration with UTAS

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